

TITLE OF THE INVENTION

High Molecular Weight Silicone Compounds,
Resist Compositions, and Patterning Method

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10 This invention relates to high molecular weight
silicone compounds (or silicone polymers) suitable as base
resins in resist compositions which lend themselves to
fine processing in the manufacture of semiconductor
devices or the like; resist compositions which are
appropriate when high energy radiation such as deep UV,
KrF excimer laser radiation (248 nm), ArF excimer laser
15 radiation (193 nm), electron beam or x-ray is used as a
light source for exposure; and a patterning method.

BACKGROUND OF THE INVENTION

20 As the LSI technology tends toward higher integration
and higher speed, further refinement of pattern rules is
required. The light exposure currently employed as
versatile technology is now approaching to the essential
limit of resolution which is dictated by the wavelength of
a light source. It is generally recognized that in light
25 exposure using g-line (436 nm) or i-line (365 nm) as a
light source, a pattern rule of about 0.5 μm is the limit.
LSIs fabricated by this technique have a degree of
integration equivalent to 16 mega-bit DRAM at maximum. At
present, LSIs fabricated in the laboratory have reached
30 this stage. It is urgently required to develop a finer
patterning technique.

One of approaches for making finer patterns is to use
exposure light of a shorter wavelength in forming resist
patterns. For the mass production process of 256 mega-bit
35 (working size up to 0.25 μm) DRAM (dynamic random access
memory), active research works are now made to substitute
a KrF excimer laser of lower wavelength (248 nm) for the

i-line (365 nm) as the light source for exposure. However, for the manufacture of DRAM with a degree of integration of 1 G or greater requiring further finer processing technology (working size up to 0.2 μm), a light source of further shorter wavelength is needed. In particular, photography using an ArF excimer laser (193 nm) is now under consideration.

In the case of lithography using light of a short wavelength of 220 nm or shorter as typified by an ArF excimer laser, in order to form fine patterns, photo-resists are required to have new properties which cannot be met by conventional materials. For this reason, since Ito et al. proposed a chemically amplified positive resist composition comprising a polyhydroxystyrene resin whose hydroxyl group is protected with a tert-butoxycarbonyloxy group (t-Boc group), known as PBOCST, and a photoacid generator in the form of an onium salt, a number of high sensitivity, high resolution resist compositions have been developed. Although these resist compositions have high sensitivity and high resolution, formation of a fine pattern having a high aspect ratio is deemed difficult when the mechanical strength of the resultant pattern is taken into account.

A number of resist compositions using polyhydroxystyrene as a base resin and having sensitivity to deep-UV, electron beams and x-rays are known in the art. These resist compositions rely on a single layer resist technique although a two-layer resist technique is advantageous in forming high aspect ratio patterns on stepped substrates. Because of such outstanding problems of substrate steps, light reflection from substrates, and difficult formation of high aspect ratio patterns, the known resist compositions are far from practical use.

It is known that the two-layer resist technique is advantageous in forming high aspect ratio patterns on stepped substrates. It is also known that in order to develop two-layer resist films with conventional alkali

developers, silicone polymers having hydrophilic groups such as hydroxyl and carboxyl groups are required. Since silicone polymers having hydroxyl groups directly attached thereto, however, undergo crosslinking reaction in the presence of acid, it is difficult to apply such silanols to chemically amplified positive resist materials.

Recently, as the silicone based positive resist material capable of solving these problems, chemically amplified silicone based positive resist materials comprising polyhydroxybenzylsilsesquioxane, known as a stable alkali soluble silicone polymer, in which some phenolic hydroxyl groups are protected with t-Boc groups, and photoacid generators combined therewith were proposed (Japanese Patent Application Kokai (JP-A) No. 118651/1995 and SPIE, Vol. 1952 (1993), 377).

However, the polymers used in these silicone resist materials have aromatic rings, which cause substantial light absorption at a wavelength of 220 nm or shorter. Thus these prior art resins as such cannot be applied to photography using light of a short wavelength of 220 nm or shorter. Since the majority of exposure light is absorbed at the surface of resist, exposure light does not penetrate through the resist to the substrate, failing to form a fine resist pattern. (See Sasago et al., "ArF Excimer Laser Lithography (3) - Resist Rating -," the preprint of the 35th Applied Physics Society Related Union Meeting, 1P-K4 (1989)).

One exemplary phenyl group-free base resin for silicone based positive resist materials is disclosed in JP-A 323611/1993. Since all hydrophilic groups such as carboxyl and hydroxyl groups necessary to enable alkali development have been protected in this base polymer, many protective groups must be decomposed before exposed areas can be dissolved in the developer. Then the amount of photoacid generator added to this end is increased and the sensitivity is exacerbated. In addition, the decomposition of many protective groups has the high

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possibility of causing a change of film thickness and generating stresses or bubbles in the film. A resist material having high sensitivity and suited for fine patterning is not available.

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SUMMARY OF THE INVENTION

An object of the invention is to provide a novel silicone polymer useful as a base resin of a positive resist composition which has a high sensitivity and resolution, is advantageously applicable to the two-layer resist technique suitable for forming high aspect ratio patterns, and can form a heat resistant pattern; a resist composition comprising the polymer as a base resin; and a pattern forming method.

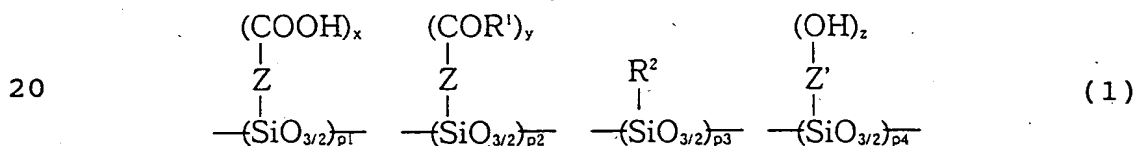
10 We have found that a high molecular weight silicone compound (often simply referred to as silicone polymer) comprising recurring units of the general formula (1) shown below and having a weight average molecular weight of 1,000 to 50,000, or a high molecular weight silicone compound in which some or all of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups in the silicone compound of formula (1) are replaced by acid labile groups of at least one type, as well as a positive resist composition comprising the silicone polymer and a photoacid generator added thereto, or a negative resist composition comprising the silicone polymer, a photoacid generator and a compound crosslinkable under the action of acid, especially resist compositions further comprising a dissolution inhibitor in addition to the photoacid generator, and the resist compositions further comprising a basic compound are effective for increasing the dissolution contrast of resist and especially a dissolution rate after exposure; that the resist compositions further comprising a compound having a group represented by =C-COOH in a molecule is effective for improving the PED stability of resist and the edge roughness on nitride film substrates; and that the

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composition is further improved in ease of coating and storage stability by further blending an acetylene alcohol derivative. Therefore, silicone base resist compositions according to the invention have high transparency, high resolution, improved latitude of exposure, process adaptability, and practical applicability, and are very useful as ultra-LSI resist materials advantageous for precise micro-processing. The present invention is predicated on these findings.

In a first aspect, the invention provides a high molecular weight silicone compound comprising recurring units represented by the following general formula (1) and having a weight average molecular weight of 1,000 to 50,000. Some or all of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups in the silicone compound may be replaced by acid labile groups of at least one type.



Herein, Z is a divalent to hexavalent, non-aromatic, monocyclic or polycyclic hydrocarbon or bridged cyclic hydrocarbon group having 5 to 12 carbon atoms; Z' is a divalent to hexavalent, normal or branched hydrocarbon group having 1 to 20 carbon atoms or non-aromatic, monocyclic or polycyclic hydrocarbon or bridged cyclic hydrocarbon group having 3 to 20 carbon atoms, these groups may have a nitrogen, oxygen or sulfur atom interposed in a carbon-to-carbon bond, the hydrogen atom on a carbon atom may be replaced by a halogen, alkoxy, nitro, cyano or acetyl group, and a methylene group in the carbon skeleton may be replaced by a carbonyl group;

letters x, y and z are integers of 1 to 5 corresponding to the valence of Z and Z';

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$$0 < p_1/(p_1+p_2+p_3+p_4) \leq 0.9,$$

$$0 \leq p_2 / (p_1 + p_2 + p_3 + p_4) \leq 0.8,$$

$$0 \leq p_3 / (p_1 + p_2 + p_3 + p_4) \leq 0.7,$$

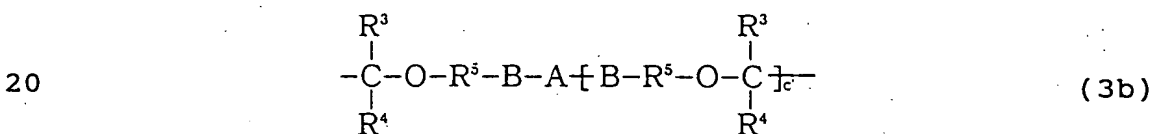
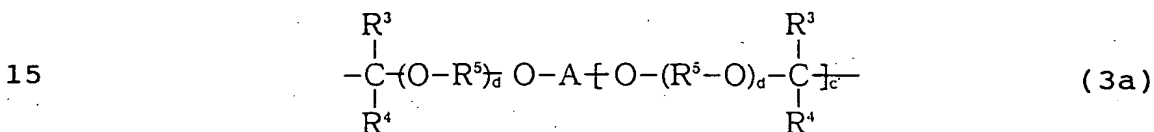
$$- \quad 0 \leq p_4 / (p_1 + p_2 + p_3 + p_4) \leq 0.9,$$

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hydrocarbon or bridged cyclic hydrocarbon groups when p1 is 0.

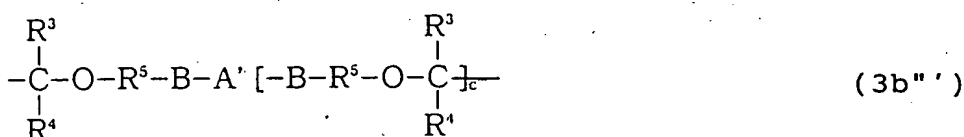
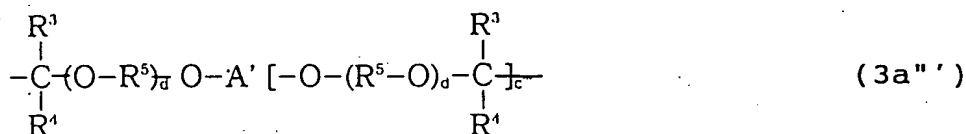
In one preferred embodiment wherein some of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups in said silicone compound are replaced by acid labile groups of at least one type,

more than 0 mol% to 50 mol% of the hydrogen atoms of the carboxyl groups and/or hydroxyl groups are replaced by crosslinking groups having C-O-C linkages represented by the following general formula (3a) or (3b) whereby the silicone compound is crosslinked within a molecule and/or between molecules.



Herein, each of R³ and R⁴ is hydrogen or a normal, branched or cyclic alkyl group of 1 to 8 carbon atoms, or R³ and R⁴, taken together, may form a ring, and each of R³ and R⁴ is a normal or branched alkylene group of 1 to 8 carbon atoms when they form a ring, R⁵ is a normal, branched or cyclic alkylene group of 1 to 10 carbon atoms, letter d is 0 or an integer of 1 to 10, A is a c-valent aliphatic or alicyclic saturated hydrocarbon group, aromatic hydrocarbon group or heterocyclic group of 1 to 50 carbon atoms, which may have an intervening hetero atom and in which the hydrogen atom attached to a carbon atom may be partially replaced by a hydroxyl group, carboxyl group, acyl group or fluorine atom, B is -CO-O-, -NHCO-O- or -NHCONH-, letter c is an integer of 2 to 8, and c' is an integer of 1 to 7.

In a further preferred embodiment, the crosslinking group having C-O-C linkages represented by the general formula (3a) or (3b) is represented by the following general formula (3a'') or (3b'').



Herein, each of R³ and R⁴ is hydrogen or a normal, branched or cyclic alkyl group of 1 to 8 carbon atoms, or R³ and R⁴, taken together, may form a ring, and each of R³ and R⁴ is a normal or branched alkylene group of 1 to 8 carbon atoms when they form a ring, R⁵ is a normal, branched or cyclic alkylene group of 1 to 10 carbon atoms, letter d is 0 or an integer of 1 to 5, A' is a c"-valent normal, branched or cyclic alkylene, alkyltriyl or alkyltetrayl group of 1 to 20 carbon atoms or arylene group of 6 to 30 carbon atoms, which may have an intervening hetero atom and in which the hydrogen atom attached to a carbon atom may be partially replaced by a hydroxyl group, carboxyl group, acyl group or fluorine atom, B is -CO-O-, -NHCO-O- or -NHCONH-, letter c" is an integer of 2 to 4, and c"" is an integer of 1 to 3.

In a further preferred embodiment, the acid labile group is at least one group selected from the class consisting of groups of the following general formula (4), groups of the following general formula (5), tertiary alkyl groups of 4 to 20 carbon atoms, trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms, and oxoalkyl groups of 4 to 20 carbon atoms.

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10 Herein, R⁶ and R⁷ each are hydrogen or a normal,
branched or cyclic alkyl group of 1 to 18 carbon atoms, R⁸
is a monovalent hydrocarbon group of 1 to 18 carbon atoms
which may have a hetero atom, or R⁶ and R⁷, R⁶ and R⁸, or R⁷
and R⁸, taken together, may form a ring, and R⁶, R⁷ and R⁸
15 each are a normal or branched alkylene group of 1 to 18
carbon atoms when they form a ring, R⁹ is a tertiary alkyl
group of 4 to 20 carbon atoms, a trialkylsilyl group whose
alkyl groups each have 1 to 6 carbon atoms, an oxoalkyl
group of 4 to 20 carbon atoms or a group of the above
20 general formula (4), and letter a is an integer of 0 to 6.

In a second aspect, the invention provides a chemically amplified positive resist composition comprising (A) an organic solvent, (B) a base resin in the form of the high molecular weight silicone compound defined above, and (C) a photoacid generator.

In a preferred embodiment, there is provided a positive resist composition comprising (A) an organic solvent, (B) a base resin in the form of the high molecular weight silicone compound comprising recurring units represented by the above-described formula (1), some or all of the hydrogen atoms of carboxyl groups and hydroxyl groups in the silicone compounds being replaced by acid labile groups of at least one type, and (C) a photoacid generator.

35 The resist composition may further comprise (D) a
dissolution inhibitor, (E) a basic compound, (F) a

compound having a group represented by $\equiv\text{C}-\text{COOH}$ in a molecule, and/or (G) an acetylene alcohol derivative.

In a preferred embodiment, there is provided a negative resist composition comprising (A) an organic solvent, (B) a base resin in the form of the high molecular weight silicone compound comprising recurring units represented by the above-described formula (1), some of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups in the silicone compounds being optionally replaced by acid labile groups of at least one type, (C) a photoacid generator, and (H) a crosslinkable compound by the action of acid.

In a third aspect, the invention provides a method for forming a pattern comprising the steps of (i) applying the resist composition defined above onto a substrate, (ii) heat treating the coated film and then exposing it to actinic radiation having a wavelength of up to 300 nm or electron beams through a photo mask, and (iii) optionally heat treating the exposed film and developing it with a developer.

More particularly, aside from phenyl-bearing silicone polymers as disclosed in JP-A 118651/1994, we have investigated and sought for a polymer in which alkali-soluble groups are not entirely, but partially, protected with acid labile groups, and which provides a high transmittance to light in the deep-UV region and a high resolution. On the other hand, known phenyl-free silicone polymers include a silicone polymer having an ethylcarboxyl group as disclosed in JP-A 323611/1993. When a polysiloxane having hydrogen atoms is reacted with an unsaturated carboxylic acid such as methacrylic acid as in this synthesis process, it is difficult to obtain a silicone polymer as illustrated in JP-A 323611/1993 because of preferential occurrence of addition reaction at the α -position of the unsaturated carboxylic acid. Since effecting hydrosilylation reaction on polymers is difficult in a quantitative sense, it is difficult to

provide a constant supply of silicone polymer. Further, the quality control of resist is difficult.

As opposed to these polymers, a resist composition comprising a silicone polymer obtained by introducing acid labile groups into some of the carboxyl groups of an aromatic ring-free high molecular weight silicone compound is highly transmissive to light of a short wavelength of 220 nm or shorter and can form a pattern with such exposure light. The present invention is predicated on this finding.

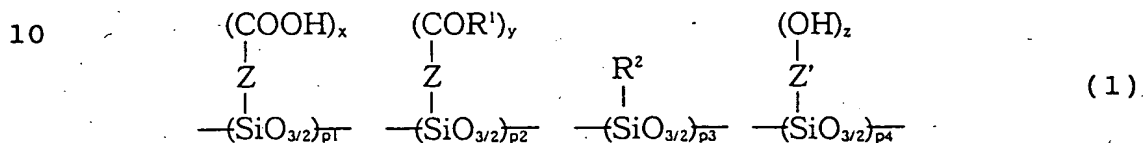
Further, a resist composition comprising a silicone polymer which has been crosslinked within a molecule and/or between molecules with crosslinking groups having C-O-C linkages resulting from reaction of some carboxyl groups therein with an alkenyl ether compound and/or halogenated alkyl ether compound exerts a dissolution inhibitory effect even in a low proportion of crosslinking and exhibits improved heat resistance on account of the increased molecular weight due to crosslinking. Additionally, since the polymer reduces its molecular weight as a result of deblocking of crosslinking groups after exposure rather than before exposure, the resist film can be increased in dissolution contrast and eventually has a high sensitivity and high resolution. Also, since the problems of footing and a difficultly soluble subsurface stratum are minimized, the resist composition allows the size and configuration of a resist pattern to be controlled as desired in terms of composition, and offers improved process adaptability. The present invention is also predicated on this finding.

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DETAILED DESCRIPTION OF THE INVENTION

Silicone polymer

The novel silicone polymer of the invention is a high molecular weight silicone compound comprising recurring units of the following general formula (1) in which acid labile groups and/or crosslinking groups optionally are incorporated.



In formula (1), Z is a di- to hexavalent, non-aromatic, monocyclic or polycyclic hydrocarbon group or bridged cyclic hydrocarbon group of 5 to 12 carbon atoms. Exemplary hydrocarbon groups are cyclopentanediy1, cyclohexanediy1, cycloheptanediy1, cyclopentanetriyl, cyclohexanetriyl, cycloheptanetriyl, cyclohexanetetrayl, cyclohexanepentayl, cyclohexanehexayl, cyclooctanediy1, cyclononanediy1, cyclodecanediy1, cyclooctanetriyl, cyclononanetriyl, cyclodecanetriyl, norbornanediy1, isobornanediy1, norbornanetriyl, isobornanetriyl, adamantanediy1, tricyclo[5,2,1,0^{2,6}]decanediy1, adamantanetriyl, tricyclo[5,2,1,0^{2,6}]decanetriyl, tricyclo[5,2,1,0^{2,6}]-decanemethylenediy1, tricyclo[5,2,1,0^{2,6}]decane-methylenetriyl, tetracyclo[4,4,0,1^{2,5},1^{7,10}]dodecanediy1, and tetracyclo[4,4,0,1^{2,5},1^{2,10}]dodecanetriyl.

Z' is a di- to hexavalent, normal or branched hydrocarbon group having 1 to 20 carbon atoms or a di- to hexavalent, non-aromatic, monocyclic or polycyclic hydrocarbon or bridged cyclic hydrocarbon group having 3 to 20 carbon atoms. These groups may have a nitrogen, oxygen or sulfur atom interposed in a carbon-to-carbon bond. The hydrogen atom on a carbon atom may be replaced by a halogen, alkoxy, nitro, cyano or acetyl group. A

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methylene group in the carbon skeleton may be replaced by a carbonyl group.

Examples of the di- to hexavalent, normal or branched hydrocarbon group having 1 to 20 carbon atoms include
5 alkyl and alkenyl groups from which the hydrogen atom attached to a carbon atom is eliminated in a number corresponding to the valence M and equal to the valence M minus 1, that is, in a number of (M - 1). For the
divalent groups, for example, alkylene and alkenylene
10 groups are exemplary. Understandably, in the case of a hydrocarbon group having 1 carbon atom, the maximum valence is 4. Unsaturated hydrocarbon groups having 2 carbon atoms also have a maximum valence of 4.

The variants of Z' are described in more detail.
15 Where a nitrogen atom is interposed in a carbon-to-carbon bond, it may take the form of -C-NH-C-. Similarly, oxygen and sulfur atoms are interposed in the form of -C-O-C- and -C-S-C-, respectively. As the substitute for the hydrogen atom on a carbon atom, examples of the halogen atom
20 include F, Cl and Br, examples of the alkoxy group include alkoxy groups of 1 to 6 carbon atoms such as methoxy, ethoxy, propoxy, isopropoxy, n-butyloxy, isobutyloxy, and tert-butyloxy. The replacement of a methylene group in the carbon skeleton by a carbonyl group is exemplified by
25 the conversion of -CH₂-CH₂-CH₂- to -CH₂-C(=O)-CH₂-.

Illustrative groups of Z' are methylene, ethylene, propanediyl, butanediyl, pentanediyl, hexanediyl, heptanediyl, octanediyl, nonanediyl, decanediyl, isopropanediyl, isobutanediyl, sec-butanediyl, tert-
30 butanetriyl, isopentanediyl, neopentanetriyl, vinyl, allyl, propenediyl, butenediyl, hexenediyl, cyclopentanediyl, cyclopentenediyl, cyclohexanediyl, cyclohexenediyl, cycloheptanediyl, cyclopentanetriyl, cyclohexanetriyl, cycloheptanetriyl, cyclohexanetetrayl,
35 cyclohexanepentayl, cyclohexanehexayl, cyclooctanediyl, cyclononanediyl, cyclodecanediyl, cyclooctanetriyl, cyclononanetriyl, cyclodecanetriyl,

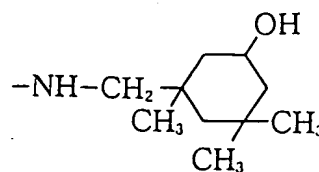
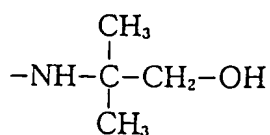
cyclopentanemethylenediyl, cyclohexanemethylenediyl,
cyclohexane-4,4-dimethylenetriyl, norbornanediyl,
isobornanediyl, norbornanetriyl, isobornanetriyl,
norbornane-5,5-dimethylenetriyl, adamantanediyl,
5 adamantanemethylenediyl, adamantanetriyl,
adamantanemethylenetriyl, tricyclo[5,2,1,0^{2,6}]decanediyl,
tricyclo[5,2,1,0^{2,6}]decanetriyl, tricyclo[5,2,1,0^{2,6}]-
decanemethylenediyl, tricyclo[5,2,1,0^{2,6}]-
decanemethylenetriyl, tetracyclo[4,4,0,1^{2,5},1^{7,10}]-
10 dodecanediyl, and tetracyclo[4,4,0,1^{2,5},1^{7,10}]dodecanetriyl.

Letters x, y and z are integers of 1 to 5
corresponding to the valence of Z and Z', preferably 1 to
3, and more preferably 1 or 2.

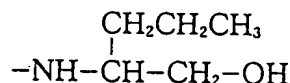
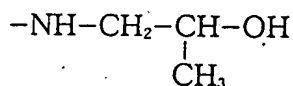
R¹ is a group represented by the following general
15 formula (2a) or (2b).



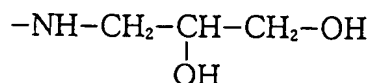
Herein, R is hydrogen, hydroxyl or a normal, branched
or cyclic alkyl group having 1 to 20 carbon atoms,
preferably 1 to 10 carbon atoms, most preferably 1 to 6
carbon atoms. R' is a normal, branched or cyclic alkylene
30 group having 1 to 20 carbon atoms, preferably 1 to 10
carbon atoms, most preferably 1 to 6 carbon atoms. These
alkyl and alkylene groups may have an oxygen atom
interposed in a carbon-to-carbon bond. Some of the
hydrogen atoms attached to carbon atoms may be replaced by
35 hydroxyl groups. Alternatively, R and R', taken together,
may form a ring, and each of R and R' is a normal or



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In formula (1), R² is a normal, branched or cyclic, substituted or unsubstituted, alkyl or alkenyl group having 1 to 8 carbon atoms or a monovalent, non-aromatic, polycyclic hydrocarbon or bridged cyclic hydrocarbon group having 5 to 12 carbon atoms. When p₁ is 0, at least some of R² groups are monovalent, non-aromatic, polycyclic hydrocarbon or bridged cyclic hydrocarbon groups.

Examples of the normal, branched or cyclic, unsubstituted alkyl or alkenyl group having 1 to 8 carbon atoms represented by R² include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, cyclohexyl, cyclopentyl, vinyl, allyl, propenyl, butenyl, hexenyl, and cyclohexenyl. Examples of the substituted alkyl or alkenyl group are those obtained by replacing some or all of the hydrogen atoms in these unsubstituted alkyl or alkenyl groups by cyano, nitro and alkoxy groups of 1 to 5 carbon atoms. Similarly, examples of the monovalent, non-aromatic, polycyclic hydrocarbon or bridged cyclic hydrocarbon group having 5 to 12 carbon atoms include cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, cycloheptyl, cycloheptenyl, cyclooctyl, cyclononanyl, cyclodecanyl, norbornanyl, norbornenyl, isobornanyl, adamantyl, adamantylmethylene, tricyclo[5,2,1,0^{2,6}]decanyl, tricyclo[5,2,1,0^{2,6}]decenyl, tricyclo[5,2,1,0^{2,6}]decanemethylene, tetracyclo[4,4,0,1^{2,5},1^{7,10}]dodecanyl, and tetracyclo[4,4,0,1^{2,5},1^{7,10}]dodecenyl.

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In formula (1), letter p1 is a positive number and p2, p3 and p4 are 0 or positive numbers and satisfy: $p1+p2+p3+p4 = 1$. That is, p1, p2, p3 and p4 represent the proportions of recurring units affixed with p1, p2, p3, and p4 in the inventive compound, respectively. These letters satisfy: $0 \leq p3/(p1+p2+p3+p4) \leq 0.7$, preferably $0 \leq p3/(p1+p2+p3+p4) \leq 0.6$, and more preferably $0 \leq p3/(p1+p2+p3+p4) \leq 0.5$. If this value is in excess of 0.7, the siloxane polymer becomes alkali insoluble and inappropriate as a base polymer for resist. Also, with too small values of $p3/(p1+p2+p3+p4)$, heat resistance is sometimes low.

These letters further satisfy:

$0 < p1/(p1+p2+p3+p4) \leq 0.9$, preferably $0.1 \leq p1/(p1+p2+p3+p4) \leq 0.85$, more preferably $0.2 \leq p1/(p1+p2+p3+p4) \leq 0.8$;
 $0 \leq p2/(p1+p2+p3+p4) \leq 0.8$, preferably $0 \leq p2/(p1+p2+p3+p4) \leq 0.6$, more preferably $0 \leq p2/(p1+p2+p3+p4) \leq 0.5$; and
 $0 \leq p4/(p1+p2+p3+p4) \leq 0.9$, preferably $0 \leq p4/(p1+p2+p3+p4) \leq 0.9$, more preferably $0.1 \leq p4/(p1+p2+p3+p4) \leq 0.85$, most preferably $0.2 \leq p4/(p1+p2+p3+p4) \leq 0.8$.

If p1 is 0, the contrast of alkali dissolution rate would become low, resulting in a poor resolution. If p1 is in excess of 0.9, it may sometimes occur that alkali solubility is lost, the film thickness changes and stresses or bubbles generate in the film during alkali development, and adhesion to the substrate is lost due to fewer hydrophilic groups.

The high molecular weight silicone compound of the invention is a polymer comprising recurring units represented by above formula (1) and having a weight

average molecular weight of 1,000 to 50,000, wherein some or all of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups may optionally be replaced by acid labile groups and/or crosslinking groups of at least one type.

The acid labile groups may be selected from a variety of acid labile groups, and are preferably groups of one or more types selected from groups of the following general formulae (4) and (5); tert-alkyl groups of 4 to 20 carbon atoms, trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms, and oxoalkyl groups of 4 to 20 carbon atoms.

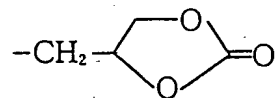
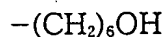
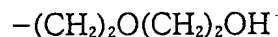
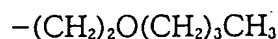


In the formulae, R^6 and R^7 each are a hydrogen atom or normal, branched or cyclic alkyl group having 1 to 18 carbon atoms, preferably 1 to 6 carbon atoms, more preferably 1 to 5 carbon atoms. R^8 is a monovalent hydrocarbon group of 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, which may have a hetero atom such as oxygen. Alternatively, R^6 and R^7 , R^6 and R^8 , or R^7 and R^8 , taken together, may form a ring, with the proviso that R^6 , R^7 and R^8 each are a normal or branched alkylene group having 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, when they form a ring. R^9 is a tertiary alkyl group having 4 to 20 carbon atoms, preferably 4 to 15 carbon atoms, more preferably 4 to 10 carbon atoms, a trialkylsilyl group whose alkyl groups

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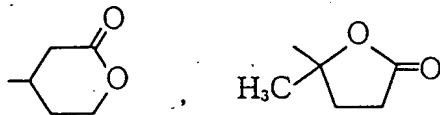
5 The normal, branched or cyclic alkyl groups of 1 to 18 carbon atoms represented by R^6 and R^7 are the same as described for R^1 .

20



Examples of the tertiary alkyl group of 4 to 20 carbon atoms represented by R⁹ include tert-butyl, 1-methylcyclohexyl, 2-(2-methyl)adamantyl and tert-amyl groups.

Examples of the trialkylsilyl group whose alkyl groups each have 1 to 6 carbon atoms include trimethylsilyl, triethylsilyl and dimethyl-tert-butyl groups. Examples of the oxoalkyl group of 4 to 20 carbon atoms include 3-oxocyclohexyl and groups of the following formulae.



10

Examples of the acid labile group of the above formula (4) include linear or branched acetal groups such as 1-methoxyethyl, 1-ethoxyethyl, 1-n-propoxyethyl, 1-isopropoxyethyl, 1-n-butoxyethyl, 1-isobutoxyethyl, 1-sec-butoxyethyl, 1-tert-butoxyethyl, 1-tert-amxyloxyethyl, 1-ethoxy-n-propyl, 1-cyclohexyloxyethyl, methoxypropyl, ethoxypropyl, 1-methoxy-1-methylethyl, and 1-ethoxy-1-methylethyl; and cyclic acetal groups such as tetrahydrofuranyl and tetrahydropyranyl, with the ethoxyethyl, butoxyethyl and ethoxypropyl groups being preferred. Examples of the acid labile group of the above formula (5) include tert-butoxycarbonyl, tert-butoxycarbonylmethyl, tert-amxyloxycarbonyl, tert-amxyloxycarbonylmethyl, 1-ethoxyethoxycarbonylmethyl, 2-tetrahydropyranyloxy-carbonylmethyl, and 2-tetrahydrofuranyloxy-carbonylmethyl groups.

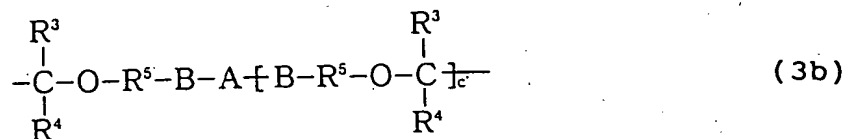
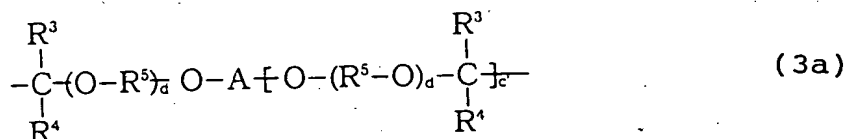
When the silicone polymer of formula (1) is used as a base resin of a positive resist composition, the percent introduction of the acid labile group is preferably more than 0 mol% to 100 mol%, more preferably 20 to 98 mol%, and further preferably 30 to 95 mol%, of the entire hydrogen atoms of carboxyl groups in the silicone polymer of formula (1) and 0 to 100 mol%, more preferably 0 to 80 mol%, and further preferably 0 to 60 mol% of the entire hydrogen atoms of hydroxyl groups in the silicone polymer of formula (1). If the hydrogen atoms of carboxyl groups

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are not replaced by acid labile groups (that is, the percent introduction of acid labile groups into the hydrogen atoms of carboxyl groups is 0 mol%), the contrast of alkali dissolution rate becomes lower, resulting in a poor resolution.

When the silicone polymer of formula (1) is used as a base resin of a negative resist composition, the percent introduction of the acid labile group is preferably 0 to 90 mol%, more preferably 0 to 80 mol%, and further preferably 0 to 70 mol%, of the entire hydrogen atoms of carboxyl group in the silicone polymer of formula (1) and 0 to 70 mol%, more preferably 0 to 60 mol%, and further preferably 0 to 50 mol% of the entire hydrogen atoms of hydroxyl groups in the silicone polymer of formula (1).

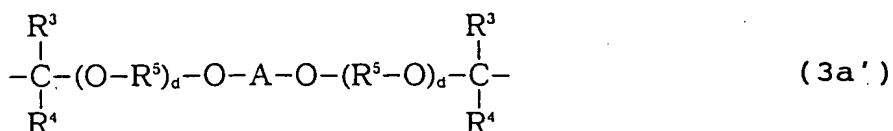
In the silicone polymer of formula (1) according to the invention, some or all of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups are replaced by acid labile groups of at least one type; and when some are replaced, more than 0 mol% to 50 mol%, more preferably 0.2 to 40 mol%, and further preferably 0.25 to 30 mol% of the hydrogen atoms of the carboxyl groups and/or hydroxyl groups may be replaced by crosslinking groups having C-O-C linkages represented by the following general formula (3a) or (3b) whereby the silicone polymer is crosslinked within a molecule and/or between molecules.

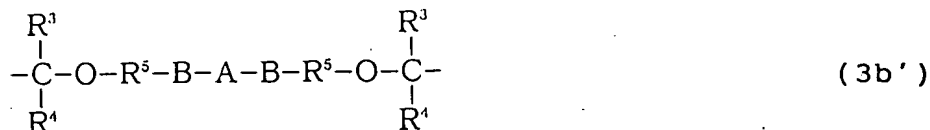


In these formulae, R³ and R⁴ each are hydrogen or a normal, branched or cyclic alkyl group of 1 to 8 carbon atoms. Alternatively, R³ and R⁴, taken together, may form a ring, with the proviso that each of R³ and R⁴ is a normal or branched alkylene group of 1 to 8 carbon atoms when they form a ring. R⁵ is a normal, branched or cyclic alkylene group of 1 to 10 carbon atoms. Letter d is 0 or an integer of 1 to 10. A is a c-valent aliphatic or alicyclic saturated hydrocarbon group, aromatic hydrocarbon group or heterocyclic group of 1 to 50 carbon atoms, which may have an intervening hetero atom and in which the hydrogen atom attached to a carbon atom may be partially replaced by a hydroxyl group, carboxyl group, acyl group or fluorine atom. B is -CO-O-, -NHCO-O- or -NHCONH-. Letter c is an integer of 2 to 8, and c' is an integer of 1 to 7.

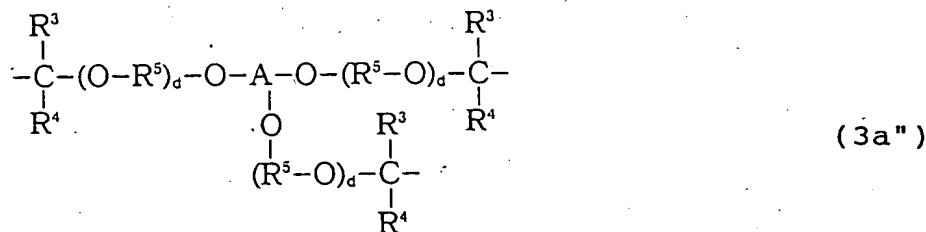
Herein, the normal, branched or cyclic alkyl groups of 1 to 8 carbon atoms are as exemplified above. The normal, branched or cyclic alkylene groups of 1 to 10 carbon atoms represented by R⁵ include methylene, ethylene, propylene, isopropylene, n-butylene, isobutylene, cyclohexylene and cyclopentylene. Examples of the group represented by A are described later. These crosslinking groups of formulae (3a) and (3b) originate from alkenyl ether compounds and halogenated alkyl ether compounds to be described later.

As understood from the value of c' in formula (3a) or (3b), the crosslinking group is not limited to a divalent one and trivalent to octavalent groups are acceptable. For example, the divalent crosslinking group is exemplified by groups of the following formulae (3a') and (3b') and the trivalent crosslinking group is exemplified by groups of the following formulae (3a'') and (3b'').

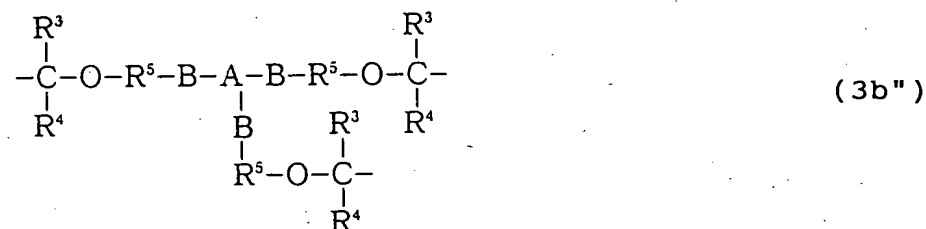




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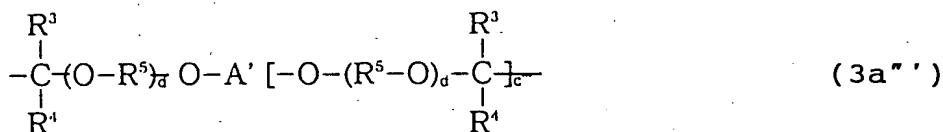


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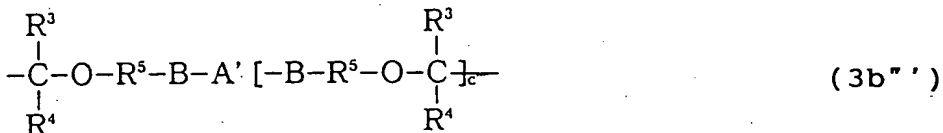


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20 Preferred crosslinking groups are of the following formulae (3a''') and (3b'''):



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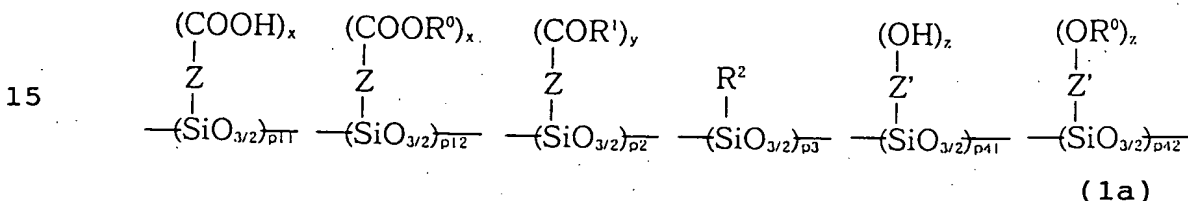


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35 wherein R³ and R⁴ each are hydrogen or a normal, branched or cyclic alkyl group of 1 to 8 carbon atoms, or R³ and R⁴, taken together, may form a ring, with the proviso that each of R³ and R⁴ is a normal or branched alkylene group of 1 to 8 carbon atoms when they form a ring, R⁵ is a normal, branched or cyclic alkylene group of 1 to 10 carbon atoms,

letter d is 0 or an integer of 1 to 5, A' is a c"-valent normal, branched or cyclic alkylene, alkyltriyyl or alkyltetrayl group of 1 to 20 carbon atoms or arylene group of 6 to 30 carbon atoms, which may have an
 5 intervening hetero atom and in which the hydrogen atom attached to a carbon atom may be partially replaced by a hydroxyl group, carboxyl group, acyl group or fluorine atom, B is -CO-O-, -NHCO-O- or -NHCONH-, letter c" is an integer of 2 to 4, and c'" is an integer of 1 to 3.

10 Preferred among the silicone polymers of the invention are silicone polymers comprising recurring units of the following general formula (1a):



Herein, Z, Z', x, y, z, R¹, R², p1, p2, p3 and p4 are
 20 as defined above, and R⁰ is an acid labile group as described above. Letters p11 and p12 are p11 + p12 = p1, p11 ≥ 0 and p12 > 0, preferably 0 < p12/p1 ≤ 1, more preferably 0.2 ≤ p12/p1 ≤ 0.98, further preferably 0.3 ≤ p12/p1 ≤ 0.95. Letters p41 and p42 are p41 + p42 = p4,
 25 p41 > 0, p42 ≥ 0. It is preferred that 0 < (p12+p42)/(p1+p4) ≤ 1, more preferably 0.05 ≤ (p12+p42)/(p1+p4) ≤ 0.9, further preferably 0.1 ≤ (p12+p42)/(p1+p4) ≤ 0.8.

30 Examples of the silicone polymers with crosslinking groups having C-O-C linkages are those represented by the following formulae (1b) to (1e). These are examples wherein x, y and z each are equal to 1. Formulae (1b) and (1d) show an intermolecular linkage and formulae (1c) and (1e) show an intramolecular linkage. The silicone

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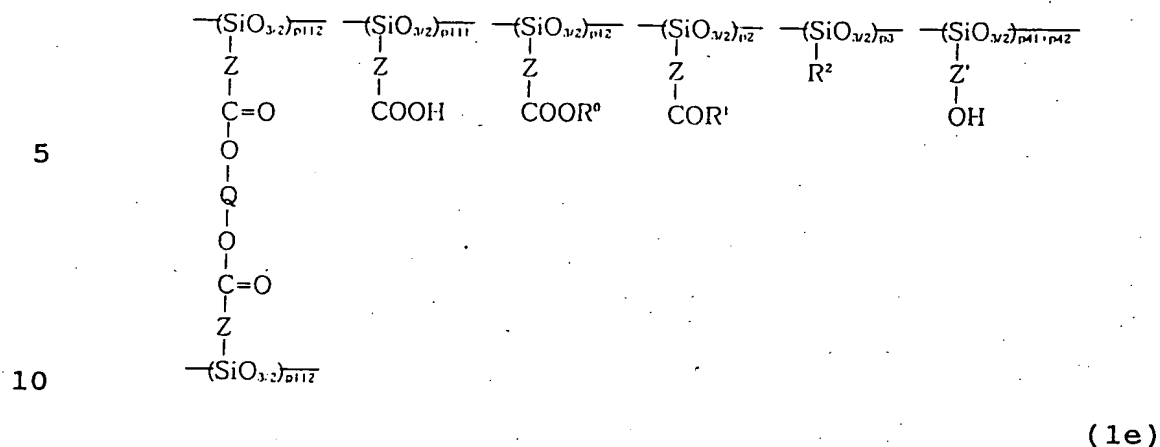
polymers of the invention are not limited to these examples.

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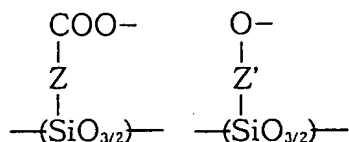
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In the above formulae, Q is a crosslinking group having a C-O-C linkage, typically a crosslinking group of formula (3a) or (3b), preferably formula (3a'), (3b'), (3a'') or (3b''), most preferably formula (3a''') or (3b'''). Where the crosslinking group is trivalent or more, Q is attached to at least three units of the following formulae in formula (1a).



In above formulae (1b) to (1e), letters preferably satisfy the relationship: $p111 + p112 = p1$, $p411 + p412 = p4$, $0 \leq p112/p1 \leq 0.5$, $0 \leq p412/p4 \leq 0.5$, $0 \leq (p112+p412)/(p1+p4) \leq 0.5$; more preferably $0.002 \leq p112/p1 \leq 0.5$, $0 \leq p412/p4 \leq 0.4$, $0.001 \leq (p112+p412)/(p1+p4) \leq 0.45$; further preferably $0.0025 \leq p112/p1 \leq 0.4$, $0 \leq p412/p4 \leq 0.3$, $0.001 \leq (p112+p412)/(p1+p4) \leq 0.4$. It is also preferred that the value of $(p12+p112+p42+p412)/(p1+p4)$ is from more than 0 to 1, more preferably 0.05 to 0.9, further preferably 0.1 to 0.8.

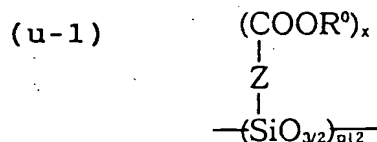
If the proportion of the crosslinking group having a C-O-C linkage is 0 mol%, no benefits of the crosslinking group are obtained, resulting in a reduced contrast of alkali dissolution rate and low resolution. If the same proportion is too high, a too much crosslinked polymer may gel, become insoluble in alkali, induce a film thickness change, internal stresses or bubbles upon alkali development, and lose adhesion to the substrate due to fewer hydrophilic groups.

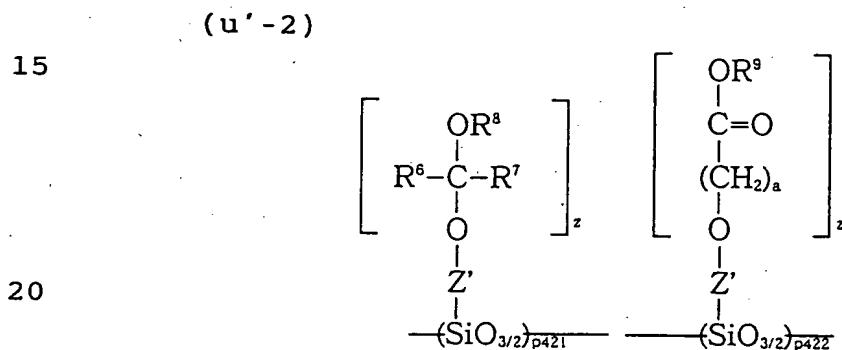
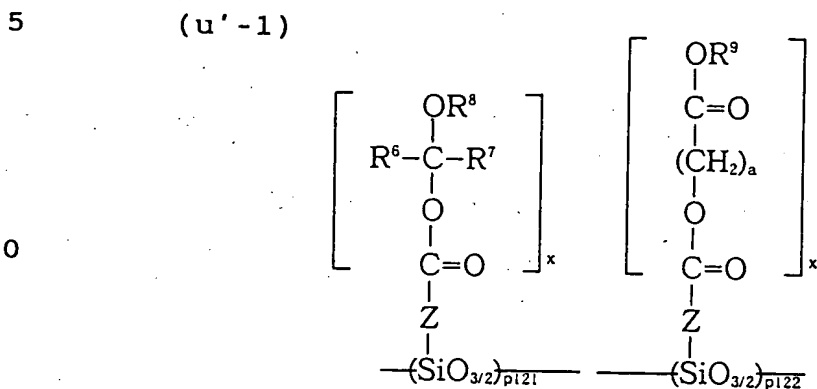
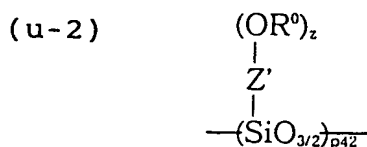
If the proportion of the acid labile group is 0 mol%, there result a reduced contrast of alkali dissolution rate and a poor resolution. If the same proportion is too high, alkali solubility may be lost and the affinity to an alkaline developer becomes low during development, resulting in a low resolution.

By properly selecting the amounts of the crosslinking group having a C-O-C linkage and the acid labile group within the above-defined ranges, the size and configuration of a resist pattern can be controlled as desired. In the silicone polymer according to the invention, the contents of the crosslinking group having a C-O-C linkage and the acid labile group have substantial influence on the dissolution rate contrast of a resist film and govern the properties of a resist composition relating to the size and configuration of a resist pattern.

Understandably, the above-mentioned silicone polymer may have acid labile groups of two or more types within its molecule, and two or more silicone polymers having different acid labile groups may be blended.

Of the acid labile group-bearing units (u-1) and (u-2) included in above formulae (1a) to (1e), the following units (u'-1) and (u'-2) are especially preferred.





In the above formulae, letters p121 and p122 are p121 + p122 = p12, p121/p12 is from 0 to 1, preferably from 0.05 to 1, more preferably from 0.1 to 1. Letters p421 and p422 are p421 + p422 = p42, p421/p42 is from 0 to 1, preferably from 0.05 to 1, more preferably from 0.1 to 1, (p121 + p421)/(p12 + p42) is from 0 to 1, preferably from 0.05 to 1, more preferably from 0.1 to 1.

The silicone polymer of the invention should have a weight average molecular weight (Mw) of 1,000 to 50,000, preferably 1,500 to 30,000. Polymers with a weight average molecular weight of less than 1,000 would provide resist materials with poor heat resistance whereas polymers with a weight average molecular weight of more than 50,000 would form resist materials which cannot be uniformly applied by spin coating.

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Preparation method

The method for preparing the silicone polymer of the above formula (1) according to the invention is now described. The silicone polymer can be prepared by

5 hydrolyzing a trichlorosilane compound bearing a di- to hexavalent, non-aromatic, mono- or polycyclic hydrocarbon group or bridged cyclic hydrocarbon group of 5 to 12 carbon atoms having an alkyl carboxylate group attached thereto, a trichlorosilane compound bearing a di- to

10 hexavalent, normal or branched hydrocarbon group of 1 to 20 carbon atoms having an alkylcarbonyloxy group attached thereto or a di- to hexavalent, non-aromatic, mono- or polycyclic hydrocarbon group or bridged cyclic hydrocarbon group of 3 to 20 carbon atoms having an alkylcarbonyloxy

15 group attached thereto, and optionally, a trichlorosilane compound having a normal, branched or cyclic alkyl group, further subjecting the hydrolytic condensate to thermal condensation, and hydrolyzing the alkyl ester group and alkyl carbonyloxy group in a conventional manner (with

20 KOH, NaOH or the like), thereby forming a silicone polymer of the following formula (1'). From the storage stability consideration, it is preferred to trimethylsilylate the polymer in order to protect silanol groups at the ends of its backbone. By introducing acid labile groups into

25 carboxyl groups of the resulting silicone polymer, the end silicone polymer can be obtained. Alternatively, by introducing the acid labile groups represented by R^0 , the groups represented by R^1 or the crosslinking groups into carboxyl groups and hydroxyl groups of the resulting

30 silicone polymer, the end silicone polymer can be obtained. The introduction of the groups represented by R^1 can be carried out by conventional procedures.

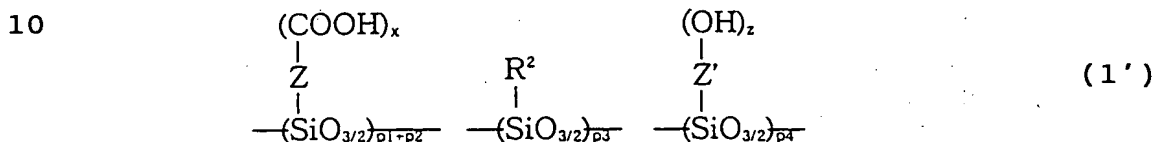
For example, when R^1 is of an ester structure as shown by-formula (2a), there may be employed a synthesis process

35 by dehydration reaction using acid catalysts, a process proceeding by way of an active ester using trifluoroacetic anhydride or dicyclohexylcarbodiimide, a process of

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activating alcohol using diethyl azodicarboxylate, and a process using O-alkylating agents such as diazoalkanes.

When R¹ is of an amide structure as shown by formula (2b), there may be employed a process using condensing agents such as dicyclohexylcarbodiimide and N-ethyl-N'-3-dimethylaminopropylcarbodiimide, a process proceeding by way of an active ester such as p-nitrophenyl ester, and an azide process proceeding by way of peptide hydrazide.



In formula (1'), Z, Z', R², p1, p2, p3, p4, x and z are as defined above.

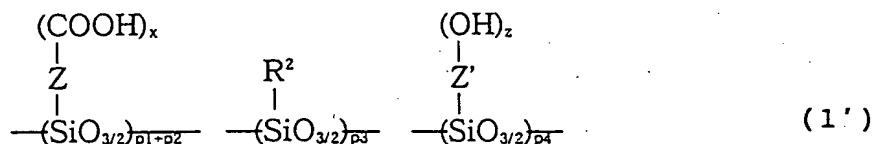
Introduction of the acid labile group can be carried out by well-known methods. For crosslinking with crosslinking groups having C-O-C linkages, methods using alkenyl ether compounds or halogenated alkyl ether compounds are useful.

More particularly, the silicone polymer bearing a crosslinking group having a C-O-C linkage according to the invention may be prepared in various ways, for example, by a method of introducing an acid labile group of the general formula (4) into a carboxyl group or a carboxyl group and a hydroxyl group of a silicone polymer (1') resulting from the above-mentioned polymerization process, isolating the polymer, and reacting it with an alkenyl ether compound or halogenated alkyl ether compound whereby the polymer is crosslinked within a molecule and/or between molecules with a crosslinking group having a C-O-C linkage; a method of reacting a silicone polymer resulting from the above-mentioned polymerization process with an alkenyl ether compound or halogenated alkyl ether compound whereby the polymer is crosslinked within a molecule and/or between molecules with a C-O-C linkage, isolating the polymer, and introducing an acid labile group of the

general formula (4) therein; or a method of carrying out reaction with an alkenyl ether compound or halogenated alkyl ether compound and introduction of an acid labile group of the general formula (4) together. The combination method of carrying out reaction with an alkenyl ether compound or halogenated alkyl ether compound and introduction of an acid labile group of the general formula (4) together is preferred. It is possible to further introduce into the thus obtained silicone polymer an acid labile group of the general formula (5), tert-alkyl, trialkylsilyl or oxoalkyl group, if necessary.

Exemplary methods include a first method using a silicone polymer comprising recurring units of the general formula (1'), an alkenyl ether compound of the general formula (I) or (II), and a compound of the general formula (4a) or a second method using a silicone polymer comprising recurring units of the general formula (1'), a halogenated alkyl ether compound of the general formula (VII) or (VIII), and a compound of the general formula (4b).

First method

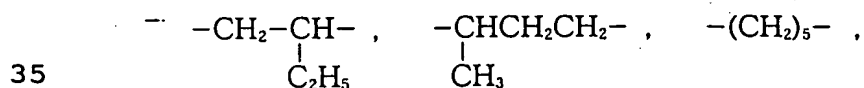
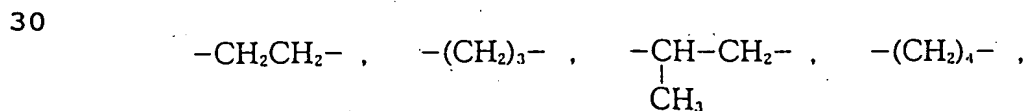


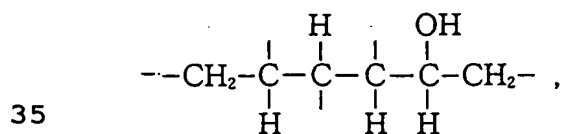
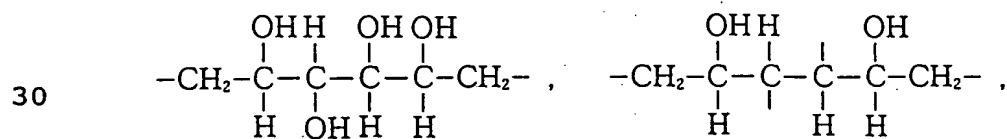
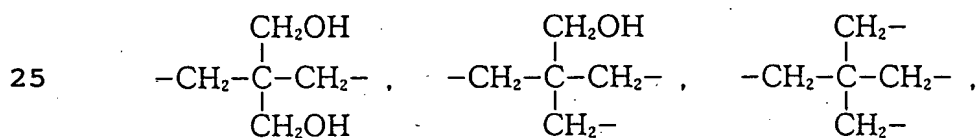
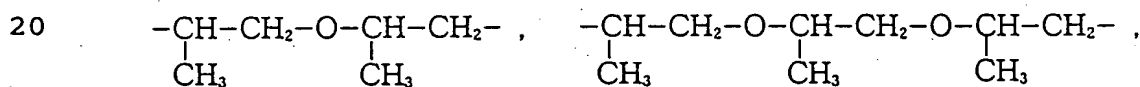
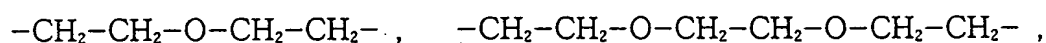
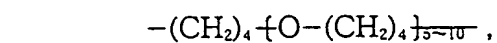
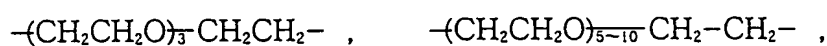
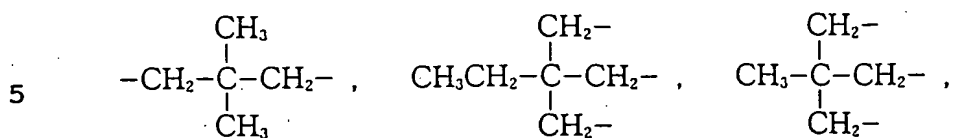
Here, Z, Z', R², p1, p2, p3, p4, x, z, R⁴, R⁵, R⁷ and R⁸ are as defined above, and R^{3a} and R^{6a} each are hydrogen or a normal, branched or cyclic alkyl group of 1 to 7 carbon atoms.

5 In the general formula (I) or (II) representing the vinyl ether compound, A is a c-valent (c is an integer of 2 to 8) aliphatic saturated hydrocarbon, alicyclic saturated hydrocarbon, aromatic hydrocarbon or heterocyclic group having 1 to 50 carbon atoms, B is
10 -CO-O-, -NHCO-O- or -NHCONH-, R⁵ is a normal or branched alkylene group of 1 to 10 carbon atoms, and letter d is 0 or an integer of 1 to 10.

Examples of the c-valent aliphatic or alicyclic saturated hydrocarbon and aromatic hydrocarbon groups
15 represented by A include substituted or unsubstituted alkylene groups having 1 to 50 carbon atoms, especially 1 to 40 carbon atoms, substituted or unsubstituted arylene groups having 6 to 50 carbon atoms, especially 6 to 40 carbon atoms (in these groups, a hetero atom such as O,
20 NH, N(CH₃), S and SO₂ may intervene and where substituted, the substituent is a hydroxyl, carboxyl, acyl group or fluorine atom), a combination of an alkylene group and an arylene group, and c"-valent groups obtained by eliminating one hydrogen atom attached to a carbon atom
25 from the foregoing groups wherein c" is an integer of 3 to 8; and c-valent heterocyclic groups, and a combination of a heterocyclic group with any one of the foregoing hydrocarbon groups.

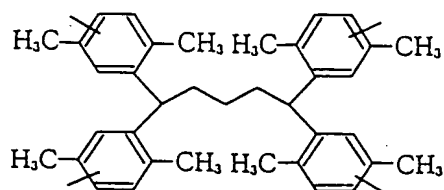
Illustrative examples of A are given below.

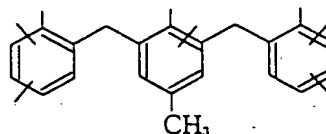
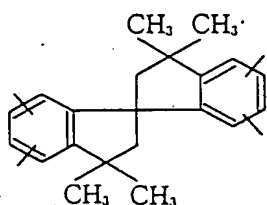
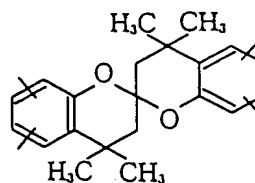
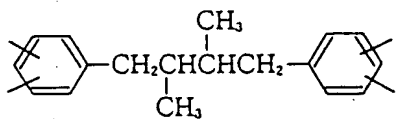




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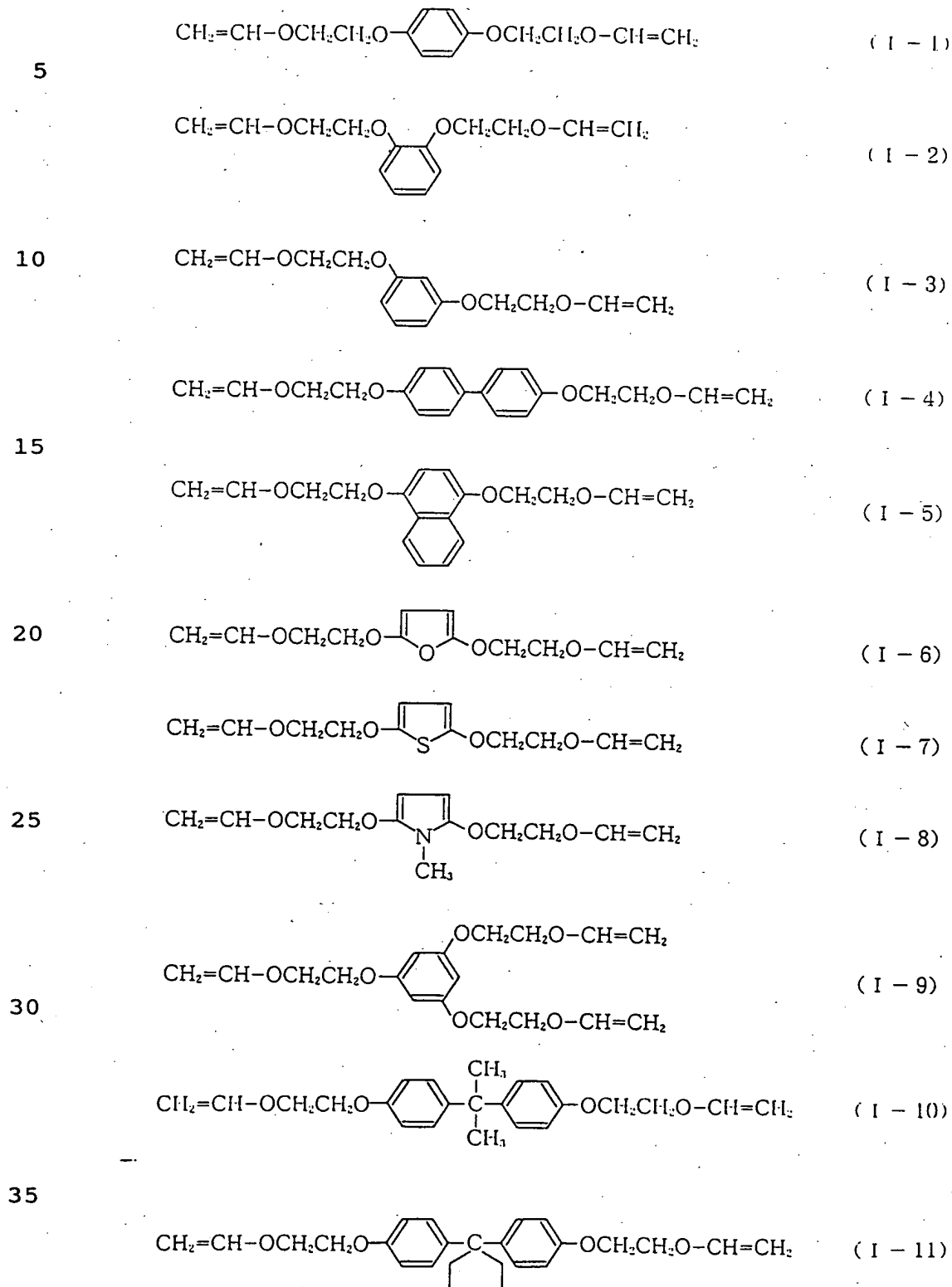


The compounds of the general formula (I) can be synthesized, for example, by the method described in Stephen C. Lapin, *Polymers Paint Colour Journal*, 179 (4237), 321 (1988), more specifically by reacting polyhydric alcohols or polyhydric phenols with acetylene or reacting polyhydric alcohols or polyhydric phenols with halogenated alkyl vinyl ethers.

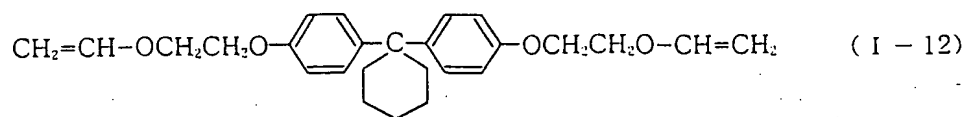
Illustrative, non-limiting examples of the compound of the general formula (I) include ethylene glycol divinyl ether, triethylene glycol divinyl ether, 1,2-propane diol divinyl ether, 1,3-propane diol divinyl ether, 1,3-butane diol divinyl ether, 1,4-butane diol divinyl ether, tetramethylene glycol divinyl ether, neopentyl glycol divinyl ether, trimethylol propane trivinyl ether, trimethylol ethane trivinyl ether, hexane diol divinyl ether, 1,4-cyclohexane diol divinyl ether, tetraethylene glycol divinyl ether, pentaerythritol divinyl ether, pentaerythritol trivinyl ether, pentaerythritol tetravinyl ether, sorbitol tetravinyl ether, sorbitol pentavinyl ether, ethylene glycol diethylene vinyl ether, triethylene glycol diethylene vinyl ether, ethylene glycol dipropylene vinyl ether, triethylene glycol diethylene vinyl ether, trimethylol propane triethylene vinyl ether, trimethylol propane diethylene vinyl ether, pentaerythritol diethylene vinyl ether, pentaerythritol triethylene vinyl ether,

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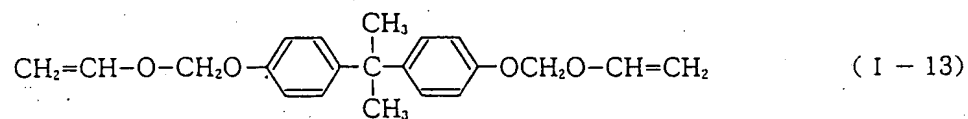
pentaerythritol tetraethylene vinyl ether as well as the compounds of the following formulae (I-1) through (I-31).



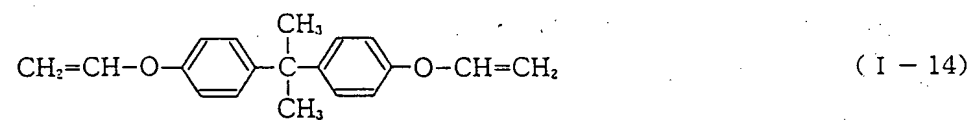
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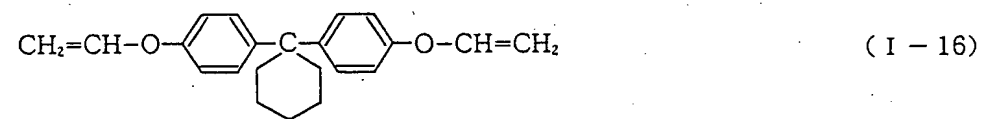
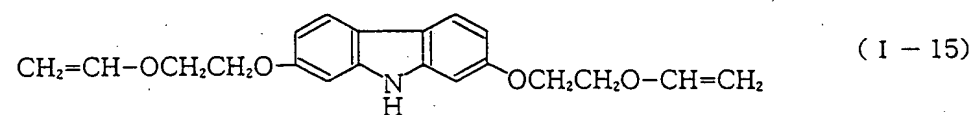
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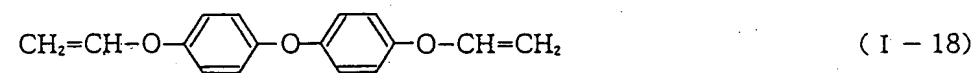
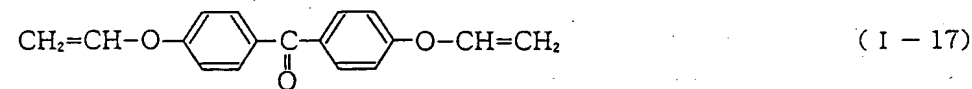
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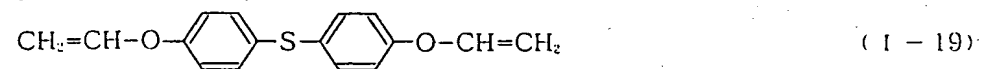
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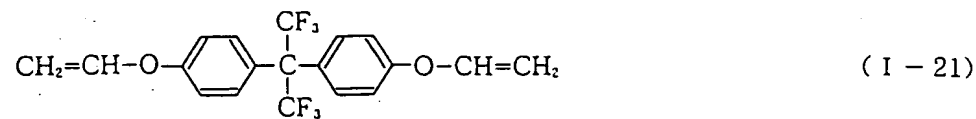
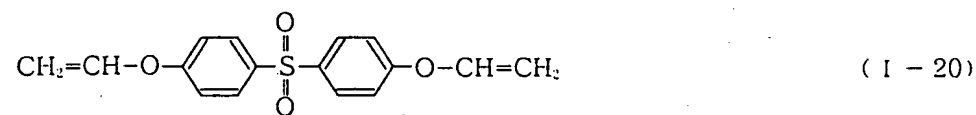
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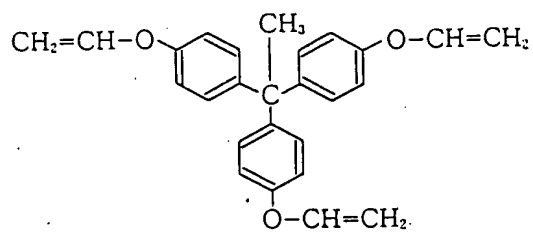
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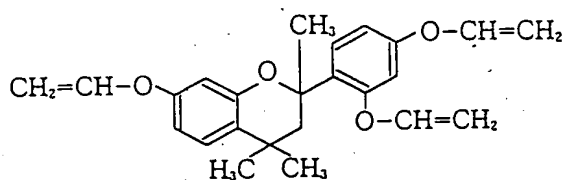
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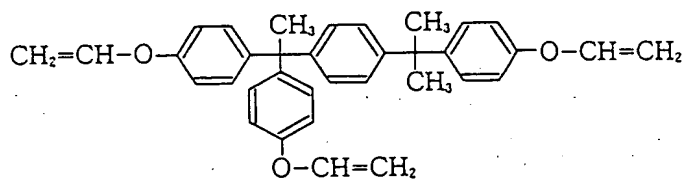
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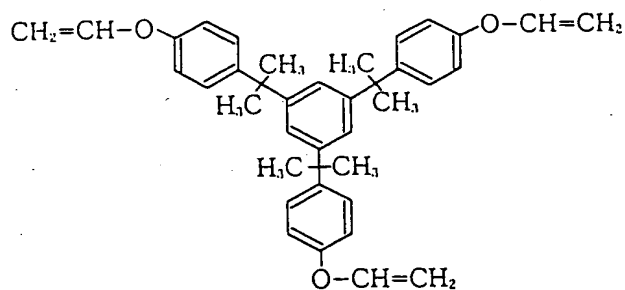
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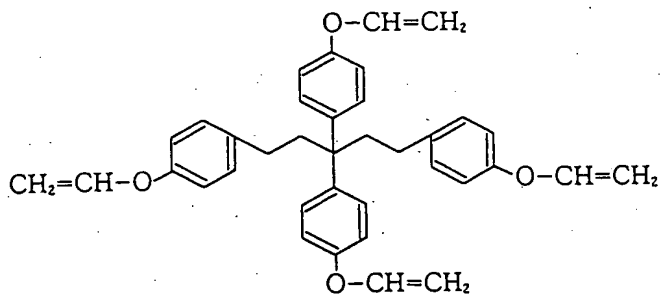
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(I - 25)

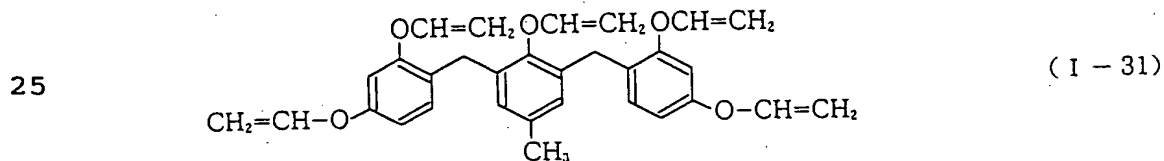
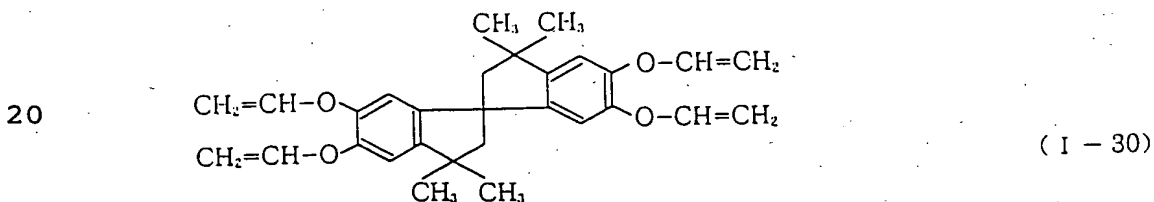
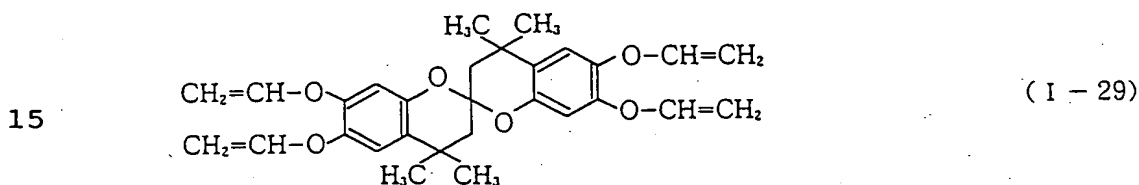
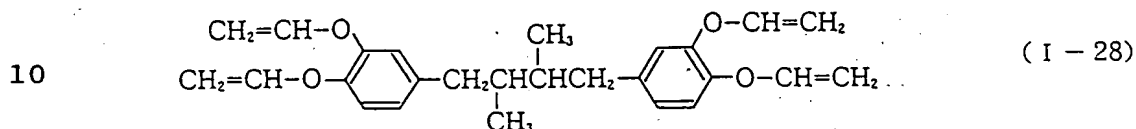
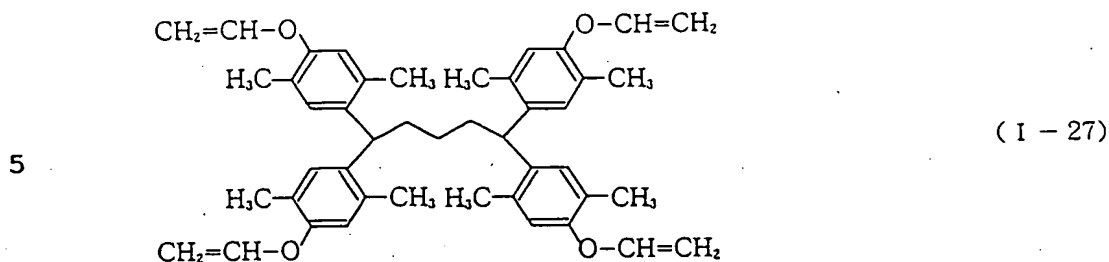
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(I - 26)

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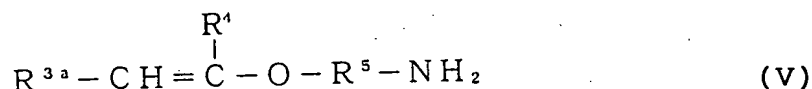
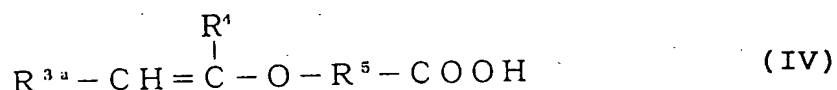
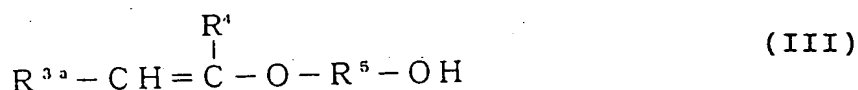
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The compounds of formula (II) wherein B is -CO-O- can be synthesized by reacting polyvalent carboxylic acids with halogenated alkyl vinyl ethers. Illustrative, non-limiting examples of the compounds of formula (II) wherein B is -CO-O- include terephthalic diethylene vinyl ether, phthalic diethylene vinyl ether, isophthalic diethylene vinyl ether, phthalic dipropylene vinyl ether, terephthalic dipropylene vinyl ether, isophthalic dipropylene vinyl ether, maleic diethylene vinyl ether,

fumaric diethylene vinyl ether, and itaconic diethylene vinyl ether.

Other useful alkenyl ether group-containing compounds which can be used herein are alkenyl ether group-containing compounds which are synthesized by reacting alkenyl ether compounds having active hydrogen as represented by the following formulae (III), (IV), and (V) with compounds having an isocyanato group.

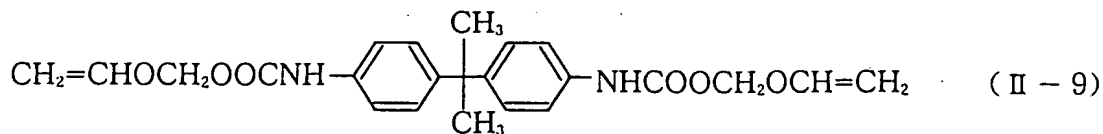
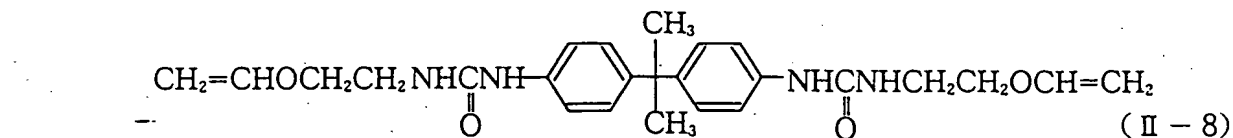
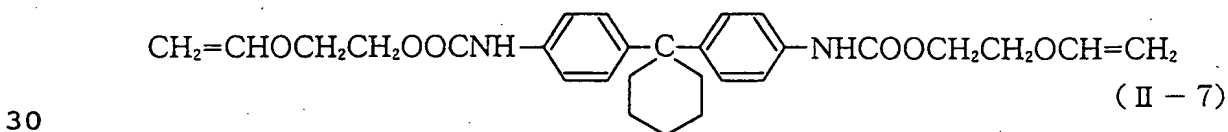
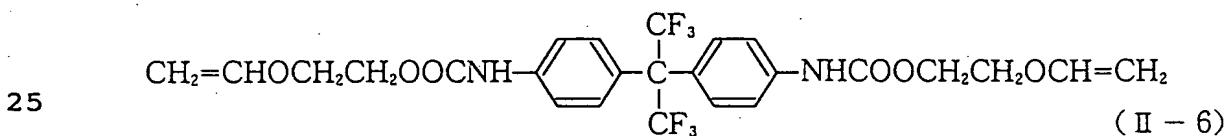
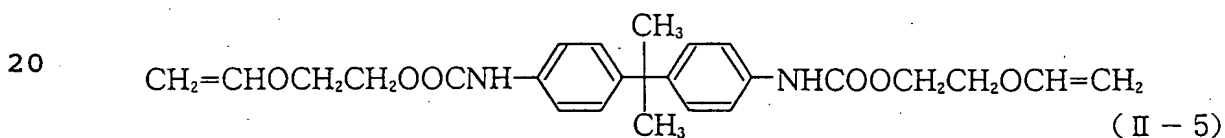
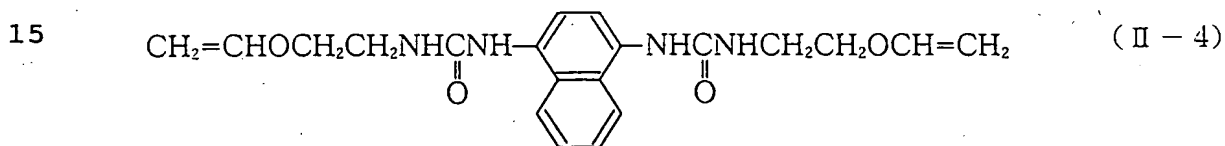
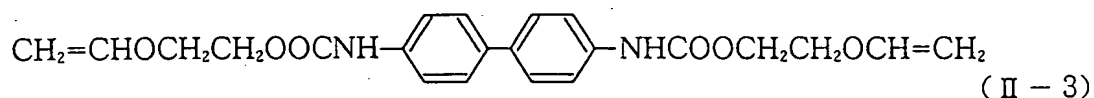
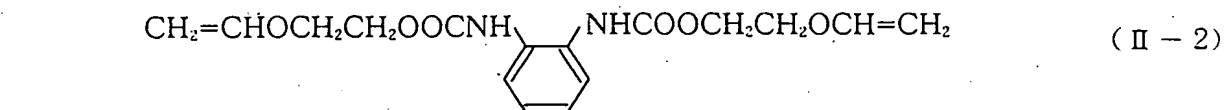
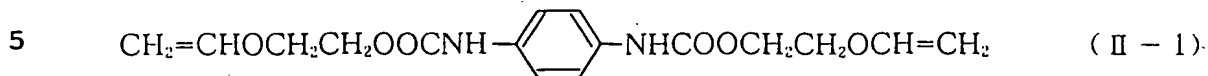


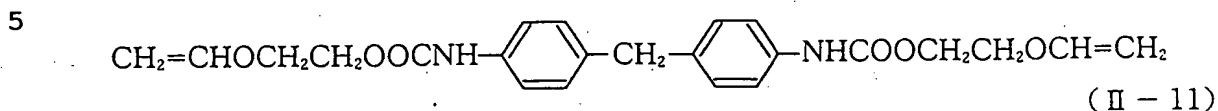
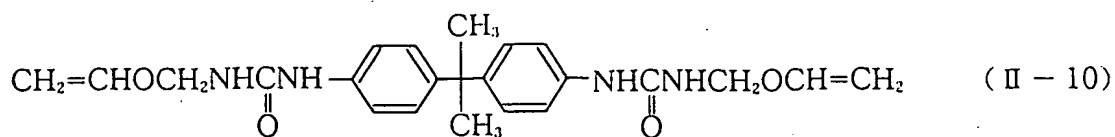
R^{3a} , R^4 , and R^5 are as defined above.

Where B is -NHCOO- or -NHCONH-, the compounds having an isocyanato group of formula (II) may be those compounds described in "Handbook of Crosslinking Agents," Taiseisha, 1981, for example. Exemplary are polyisocyanates such as triphenylmethane triisocyanate, diphenylmethane diisocyanate, tolylene diisocyanate, 2,4-tolylene diisocyanate dimer, naphthalene-1,5-diisocyanate, o-tolylene diisocyanate, polymethylene polyphenyl isocyanate, and hexamethylene diisocyanate; and polyisocyanate adducts such as an addition product of tolylene diisocyanate and trimethylolpropane, an addition product of hexamethylene diisocyanate and water, and an addition product of xylene diisocyanate and trimethylolpropane. By reacting isocyanato group-containing compounds with active hydrogen-containing alkenyl ether compounds, there are obtained various compounds having an alkenyl ether group at an end. These compounds are

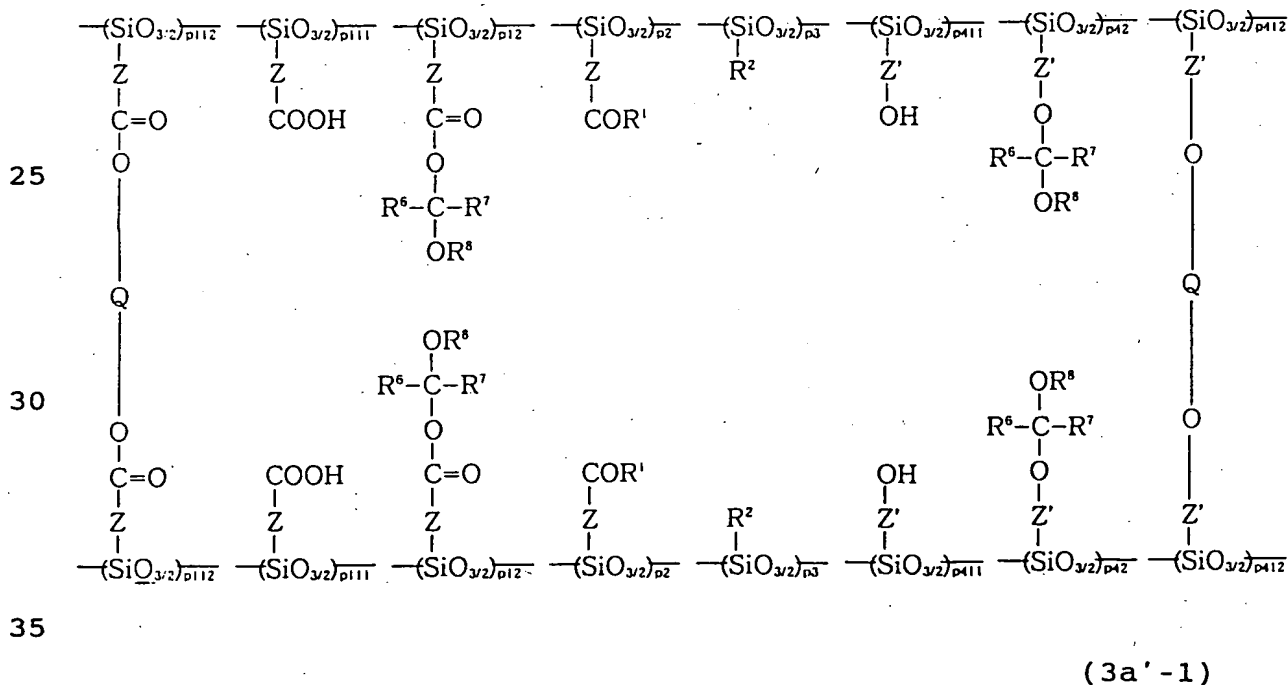
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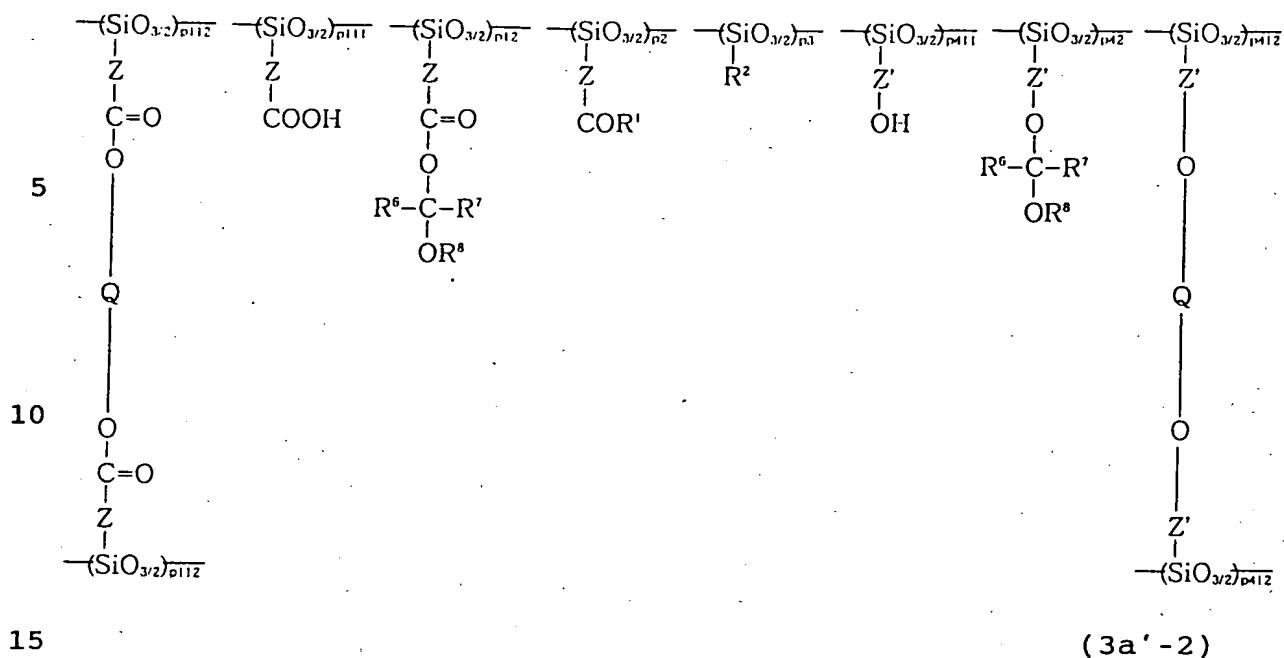
exemplified by the following formulae (II-1) through (II-11), though not limited thereto.





More particularly, when it is desired to obtain a
 10 silicone polymer crosslinked with crosslinking groups
 having C-O-C linkages according to the first method, a
 polymer having a weight average molecular weight of 1,000
 to 500,000 and preferably represented by the general
 formula (1') is reacted with p112 + p412 mol of an alkenyl
 15 ether compound of the general formula (I) or (II) and p12
 + p42 mol of a compound of the general formula (4a) per
 mol of the carboxyl group or the carboxyl and hydroxyl
 groups in the polymer of the general formula (1'), thereby
 forming a polymer of the following general formula (3a'-1)
 20 or (3a'-2), for example.





The reaction solvent used in the first method is preferably selected from aprotic polar solvents such as dimethylformamide, dimethylacetamide, tetrahydrofuran, and ethyl acetate, and mixtures thereof.

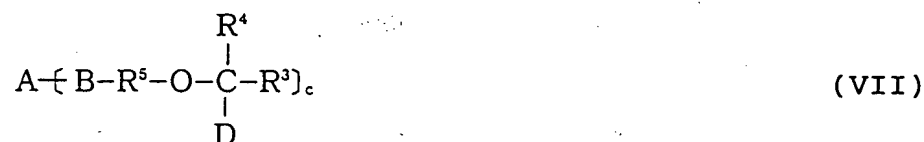
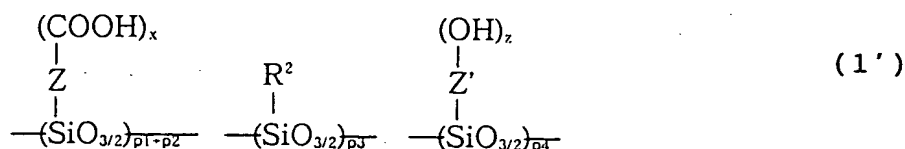
The acid catalyst used herein is preferably selected from hydrochloric acid, sulfuric acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, trifluoroacetic acid, and pyridinium p-toluenesulfonate. The amount of the acid catalyst used is preferably 0.1 to 10 mol% per mol of the carboxyl group in the polymer of the general formula (1') to be reacted.

The reaction temperature is from -20°C to 100°C, more preferably from 0°C to 60°C, and the reaction time is 0.2 to 100 hours, preferably 1/2 to 20 hours.

Where two types of reaction are carried out in a contiguous manner without once isolating an intermediate product, the order of addition of the alkenyl ether compound of the general formula (I) or (II) and the compound of the general formula (4a) is not critical. Preferably, the compound of the general formula (4a) is first added and after reaction proceeds to a full extent,

the alkenyl ether compound of the general formula (I) or (II) is added. If the alkenyl ether compound of the general formula (I) or (II) and the compound of the general formula (4a) are simultaneously added or if the alkenyl ether compound of the general formula (I) or (II) is first added, then some of reactive sites of the alkenyl ether compound of the general formula (I) or (II) can be hydrolyzed with water in the reaction system whereby there is formed a polymer of complex structure which is difficult to control its physical properties.

Second method



Herein, Z, Z', R², p1, p2, p3, p4, x, z, R⁵, R^{6a}, R⁷, R⁸, c and d are as defined above, and D is a halogen atom such as Cl, Br or I.

It is understood that the compounds of the above formulae (VI), (VII) and (4b) can be produced by reacting the compounds of the above formulae (I), (II) and (4a)

with hydrogen chloride, hydrogen bromide or hydrogen iodide, respectively.

When it is desired to obtain a crosslinked silicone polymer according to the second method, a polymer
5 comprising recurring units of the general formula (1') and having a weight average molecular weight of 1,000 to 500,000 is reacted with p112 + p412 mol of a halogenated alkyl ether compound of the general formula (VI) or (VII) and p12 + p42 mol of a compound of the general formula
10 (4b) per mol of the carboxyl group or the carboxyl and hydroxyl groups in the polymer of formula (1'), thereby forming a polymer of the above formula (3a'-1) or (3a'-2), for example.

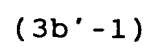
In the second method, reaction is preferably carried
15 out in a solvent in the presence of a base. The reaction solvent used herein is preferably selected from aprotic polar solvents such as acetonitrile, acetone, dimethylformamide, dimethylacetamide, tetrahydrofuran, and dimethylsulfoxide, and mixtures thereof. The base used
20 herein is preferably selected from triethylamine, pyridine, diisopropylamine and potassium carbonate. The amount of the base used is preferably at least 1 mol, especially at least 5 mol, per mol of the carboxyl group in the polymer of formula (1') to be reacted.

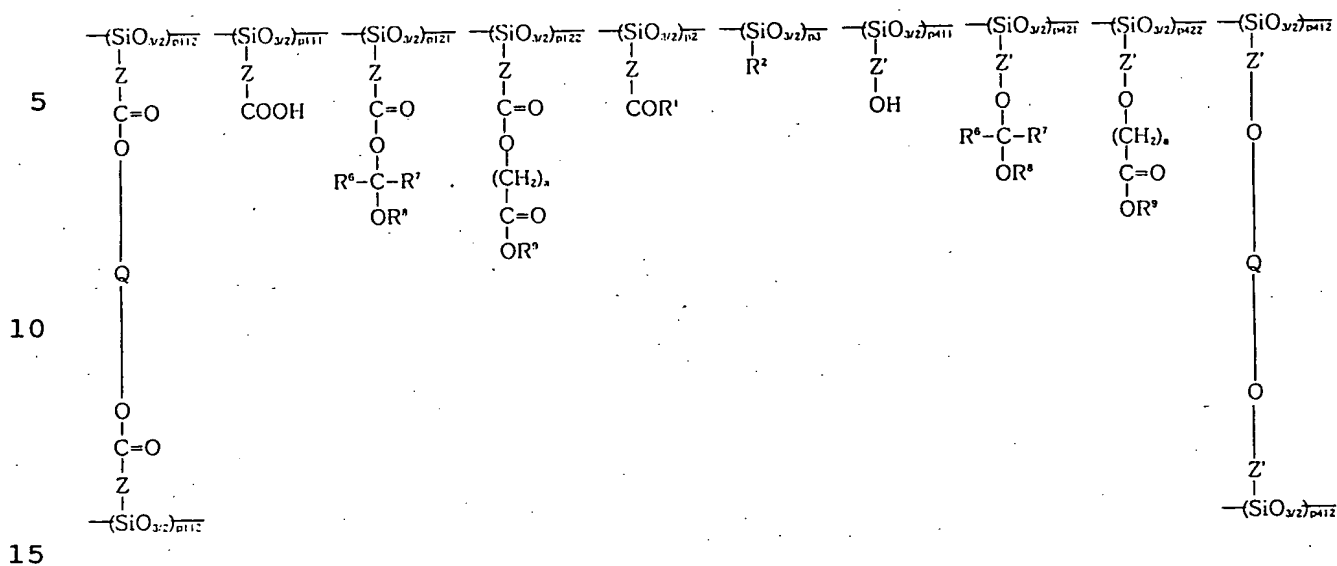
25 The reaction temperature is from -50°C to 100°C, more preferably from 0°C to 60°C, and the reaction time is from 1/2 to 100 hours, preferably from 1 to 20 hours.

It is acceptable to take a reaction sequence of first reacting a polymer having recurring units of formula (1')
30 or a modified one thereof wherein some of the carboxyl groups are replaced by COR¹ groups with a compound of formula (4a) or (4b) to form a compound having an acid labile group, for example, a compound of the following formula (1''), isolating the compound of formula (1''), and
35 then crosslinking the compound of formula (1'') using a compound of formula (I), (II), (VI) or (VII).



20





(3b'-2)

Preferably the introduction of an acid labile group of the above formula (5) is carried out in a solvent in the presence of a base. The reaction solvent used herein is preferably selected from aprotic polar solvents such as acetonitrile, acetone, dimethylformamide, dimethylacetamide, tetrahydrofuran, and dimethylsulfoxide, and mixtures thereof. The base used herein is preferably selected from triethylamine, pyridine, imidazole, diisopropylamine and potassium carbonate. The amount of the base used is preferably at least 1 mol, especially at least 5 mol, per mol of the carboxyl group in the original polymer of formula (1').

The reaction temperature is from 0°C to 100°C, more preferably from 0°C to 60°C, and the reaction time is from 0.2 to 100 hours, preferably from 1 to 10 hours.

Examples of the dialkyl dicarbonate compound include di-tert-butyl dicarbonate and di-tert-amyl dicarbonate. Examples of the alkoxycarbonylalkyl halide include tert-butoxycarbonylmethyl chloride, tert-amylloxycarbonylmethyl

chloride, tert-butoxycarbonylmethyl bromide, and tert-butoxycarbonylethyl chloride. Examples of the trialkylsilyl halide include trimethylsilyl chloride, triethylsilyl chloride, and dimethyl-tert-butylsilyl chloride.

Furthermore, if necessary, the polymer of the general formula (3a'-1) or (3a'-2) obtained by the first or second method can be tert-alkylated or oxoalkylated by reacting the polymer with p12 + p42 mol of a tert-alkylating compound or oxoalkyl compound per mol of the carboxyl group in the original polymer of formula (1').

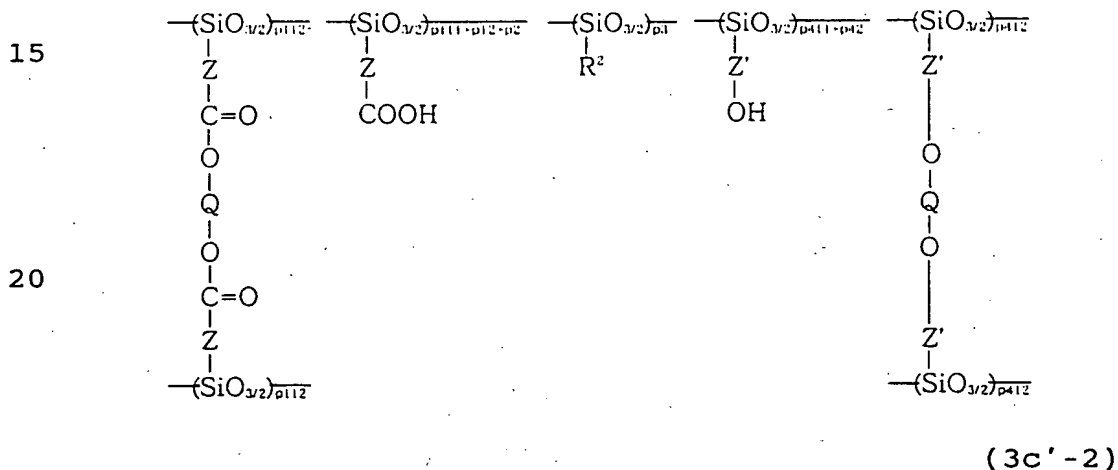
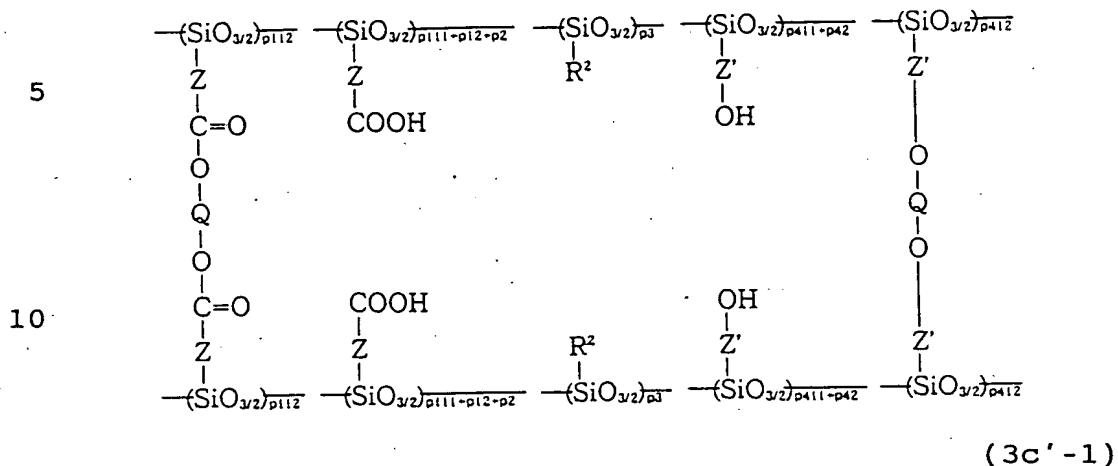
Preferably this reaction is carried out in a solvent in the presence of an acid. The reaction solvent used herein is preferably selected from aprotic polar solvents such as dimethylformamide, dimethylacetamide, tetrahydrofuran, and ethyl acetate, and mixtures thereof. The acid used herein as the catalyst is preferably selected from hydrochloric acid, sulfuric acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, trifluoroacetic acid, and pyridinium p-toluenesulfonate. The amount of the acid catalyst used is preferably 0.1 to 10 mol% per mol of the carboxyl group in the original polymer of formula (1').

The reaction temperature is from -20°C to 100°C, more preferably from 0°C to 60°C, and the reaction time is from 0.2 to 100 hours, preferably from 1/2 to 20 hours.

Exemplary tert-alkylating compounds include isobutene, 2-methyl-1-butene, and 2-methyl-2-butene. Exemplary oxoalkyl compounds include α -angelica lactone, 2-cyclohexen-1-one, and 5,6-dihydro-2H-pyran-2-one.

Apart from the route of once forming a polymer of the general formula (3a'-1) or (3a'-2), it is possible to directly introduce an acid labile group of the general formula (5), tertiary alkyl group, trialkylsilyl group or oxoalkyl group into a polymer comprising recurring units of the following general formula (3c'-1) or (3c'-2) and

optionally further introduce an acid labile group of the general formula (4).



In the polymer of the invention, the acid labile group represented by R^2 is not limited to one type. Acid labile groups of two or more types can be introduced into the polymer. A polymer having acid labile groups of two or more types can be obtained by first introducing $p41$ mol of an acid labile group per mol of the entire hydroxyl groups in the polymer of formula (1') as above, then introducing $p42$ mol of a different acid labile group by the same procedure as above, and in the case of three or more types, repeating such introduction appropriate times.

Resist composition

The silicone polymer of the invention is useful as a base resin of a resist composition. The present invention provides a resist composition comprising the silicone polymer as a base resin.

The resist composition of the invention is a positive type or a negative type. The preferred positive or negative resist composition is a chemically amplified resist composition.

A preferred chemically amplified positive resist composition comprises

(A) an organic solvent,

(B) a base resin in the form of the above-defined silicone polymer, especially the silicone polymer in which some or all of the hydrogen atoms of carboxyl groups or carboxyl groups and hydroxyl groups are replaced by acid labile groups, and

(C) an photoacid generator.

If desired, the positive resist composition may further contain the following components.

(D) dissolution inhibitor

(E) basic compound

(F) compound having a group represented by $\equiv\text{C}-\text{COOH}$ in a molecule

(G) acetylene alcohol derivative

A preferred chemically amplified negative resist composition comprises

(A) an organic solvent,

(B) a base resin in the form of the above-defined silicone polymer, especially the silicone polymer in which some of the hydrogen atoms of carboxyl group or carboxyl and hydroxyl groups may be replaced by acid labile groups,

(C) an photoacid generator, and

(D) a crosslinkable compound by the action of acid.

The organic solvent used herein as component (A) may be any desired one of organic solvents in which the photoacid generator, base resin, dissolution inhibitor and

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other components are soluble. Illustrative examples of the organic solvent include ketones such as cyclohexanone and methyl-2-n-amylketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; and esters such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, tert-butyl acetate, tert-butyl propionate, and propylene glycol mono-tert-butyl ether acetate. These solvents may be used alone or in admixture of two or more. The solvents are not limited to these examples. Of these organic solvents, diethylene glycol dimethyl ether and 1-ethoxy-2-propanol ensuring the maximum solubility of photoacid generators, propylene glycol monomethyl ether acetate ensuring safety, and mixtures thereof are preferably used.

The amount of the organic solvent used is preferably 200 to 1,000 parts, more preferably 400 to 800 parts per 100 parts of component (B). All parts are by weight, hereinafter.

The photoacid generators used as component (C) include

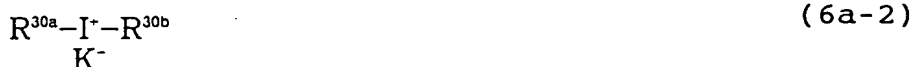
- 1) onium salts of the following general formula (6a-1), (6a-2) or (6b),
- 2) diazomethane derivatives of the following general formula (7),
- 3) glyoxime derivatives of the following general formula (8),
- 4)-bissulfone derivatives of the following general formula (9),
- 5) sulfonic acid esters of N-hydroxyimide compounds of the following general formula (10),

- 6) β -ketosulfonic acid derivatives,
- 7) disulfone derivatives,
- 8) nitrobenzylsulfonate derivatives, and
- 9) sulfonate derivatives.

5



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In the formulae, R^{30a} , R^{30b} and R^{30c} each are a normal, branched or cyclic alkyl, alkenyl, oxoalkyl or oxoalkenyl group of 1 to 12 carbon atoms, aryl group of 6 to 20 carbon atoms, or aralkyl or aryloxoalkyl group of 7 to 12 carbon atoms wherein some or all of the hydrogen atoms may be replaced by alkoxy or other groups. Alternatively, R^{30b} and R^{30c} , taken together, may form a ring with the proviso that each of R^{30b} and R^{30c} is an alkylene group of 1 to 6 carbon atoms when they form a ring. K^- is a non-nucleophilic counter ion.

R^{30a} , R^{30b} and R^{30c} may be the same or different. Illustratively stated, exemplary alkyl groups include methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclopropylmethyl, 4-methylcyclohexyl, cyclohexylmethyl, norbornyl, and adamantyl. Exemplary alkenyl groups include vinyl, allyl, propenyl, butenyl, hexenyl, and cyclohexenyl. Exemplary oxoalkyl and oxoalkenyl groups include 2-oxocyclopentyl and 2-oxocycloheptyl as well as 2-oxopropyl and 2-alkyl-2-oxoethyl groups such as 2-cyclopentyl-2-oxoethyl, 2-cyclohexyl-2-oxoethyl and 2-(4-methylcyclohexyl)-2-oxoethyl. Exemplary aryl groups are phenyl and naphthyl; alkoxyphenyl groups such as p-methoxyphenyl, m-methoxyphenyl, o-methoxyphenyl, ethoxyphenyl, p-tert-

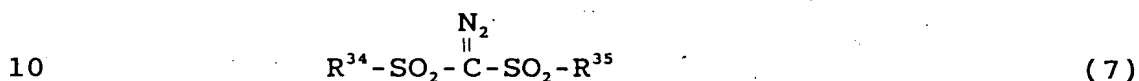
butoxyphenyl, and m-tert-butoxyphenyl; alkylphenyl groups such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, ethylphenyl, 4-tert-butylphenyl, 4-butylphenyl, and dimethylphenyl; alkyl-naphthyl groups such as methyl-naphthyl and ethyl-naphthyl; alkoxy-naphthyl groups such as methoxy-naphthyl and ethoxy-naphthyl; dialkyl-naphthyl groups such as dimethyl-naphthyl and diethyl-naphthyl; and dialkoxy-naphthyl groups such as dimethoxy-naphthyl and diethoxy-naphthyl. Exemplary aralkyl groups are benzyl, phenylethyl and phenethyl. Exemplary aryloxoalkyl groups include 2-aryl-2-oxoethyl groups such as 2-phenyl-2-oxoethyl, 2-(1-naphthyl)-2-oxoethyl and 2-(2-naphthyl)-2-oxoethyl. Examples of the non-nucleophilic counter ion represented by K⁻ include halide ions such as chloride and bromide ions; fluoroalkylsulfonate ions such as triflate, perfluorooctylsulfonate, 1,1,1-trifluoroethanesulfonate, and nonafluorobutanesulfonate; aryl-sulfonate ions such as tosylate, benzenesulfonate, 4-fluorobenzenesulfonate, 4-trifluoromethylbenzenesulfonate, and 1,2,3,4,5-pentafluorobenzenesulfonate; and alkylsulfonate ions such as mesylate and butanesulfonate.



In the formula, R^{31a} and R^{31b} each are a normal, branched or cyclic alkyl group of 1 to 8 carbon atoms, R³² is a normal, branched or cyclic alkylene group of 1 to 10 carbon atoms, R^{33a} and R^{33b} each are a 2-oxoalkyl group of 3 to 7 carbon atoms, and K⁻ is a non-nucleophilic counter ion.

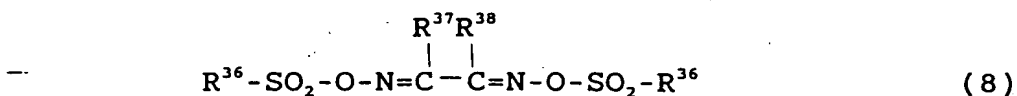
Illustrative examples of R^{31a} and R^{31b} include methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, cyclopentyl, cyclohexyl, cyclopropylmethyl, 4-methylcyclohexyl and cyclohexylmethyl groups. Illustrative examples of R³² include methylene,

ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, 1,4-cyclohexylene, 1,2-cyclohexylene, 1,3-cyclopentylene, 1,4-cyclooctylene and 1,4-cyclohexanedimethylene groups. Illustrative examples of R^{33a} and R^{33b} include 2-oxopropyl, 2-oxocyclopentyl, 2-oxocyclohexyl and 2-oxocycloheptyl groups. Examples of K are as described in conjunction with formula (6a).



In the formula, R^{34} and R^{35} are normal, branched or cyclic alkyl or halogenated alkyl groups of 1 to 12 carbon atoms, aryl or halogenated aryl groups of 6 to 20 carbon atoms, or aralkyl groups of 7 to 12 carbon atoms.

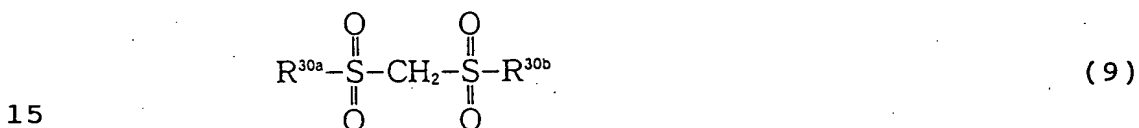
Examples of the alkyl group represented by R^{34} and R^{35} include methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, amyl, cyclopentyl, cyclohexyl, cycloheptyl, norbornyl, and adamantyl. Examples of the halogenated alkyl group include trifluoromethyl, 1,1,1-trifluoroethyl, 1,1,1-trichloroethyl, and nonafluorobutyl. Examples of the aryl group include phenyl; alkoxyphenyl groups such as p-methoxyphenyl, m-methoxyphenyl, o-methoxyphenyl, ethoxyphenyl, p-tert-butoxyphenyl, and m-tert-butoxyphenyl; and alkyl phenyl groups such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, ethylphenyl, 4-tert-butylphenyl, 4-butylphenyl, and dimethylphenyl. Exemplary halogenated aryl groups are fluorobenzene, chlorobenzene, and 1,2,3,4,5-pentafluorobenzene. Exemplary aralkyl groups are benzyl and phenethyl.



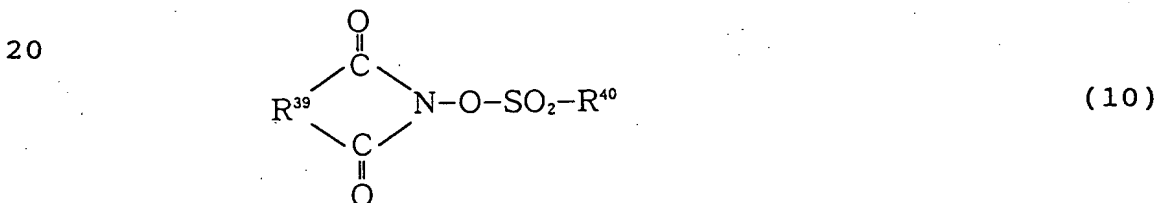
In the formula, R^{36} , R^{37} and R^{38} are normal, branched or cyclic alkyl or halogenated alkyl groups of 1 to 12 carbon

5 normal or branched alkylene group of 1 to 6 carbon atoms
when they form a cyclic structure.

Examples of the alkyl, halogenated alkyl, aryl, halogenated aryl, and aralkyl groups represented by R^{36} , R^{37} and R^{38} are the same as described for R^{34} and R^{35} . Examples of the alkylene group represented by R^{37} and R^{38} include methylene, ethylene, propylene, butylene, and hexylene.



In the formula, R^{30a} and R^{30b} are as defined above.



25 In the formula, R³⁹ represents an arylene group of 6
to 10 carbon atoms, alkylene group of 1 to 6 carbon atoms
or alkenylene group of 2 to 6 carbon atoms, wherein some
or all of the hydrogen atoms may be replaced by normal or
branched alkyl or alkoxy groups of 1 to 4 carbon atoms,
30 nitro groups, acetyl groups or phenyl groups. R⁴⁰
represents a normal, branched or substituted alkyl,
alkenyl or alkoxyalkyl group of 1 to 8 carbon atoms,
phenyl group or naphthyl group, wherein some or all of the
hydrogen atoms may be replaced by alkyl or alkoxy groups
35 of 1 to 4 carbon atoms, phenyl groups (which may be
replaced by alkyl or alkoxy groups of 1 to 4 carbon atoms,

nitro groups or acetyl groups), hetero-aromatic groups of 3 to 5 carbon atoms, or fluorine or chlorine atoms.

Exemplary arylene groups represented by R^{39} include 1,2-phenylene and 1,8-naphthylene groups; exemplary
5 alkylene groups include methylene, 1,2-ethylene, 1,3-propylene, 1,4-butylene, 1-phenyl-1,2-ethylene, and norbornane-2,3-diyl groups; and exemplary alkenylene groups include 1,2-vinylene, 1-phenyl-1,2-vinylene and 5-norbornene-2,3-diyl groups. Exemplary alkyl groups
10 represented by R^{40} are similar to R^{30a} to R^{30c} ; exemplary alkenyl groups include vinyl, 1-propenyl, allyl, 1-butenyl, 3-butenyl, isoprenyl, 1-pentenyl, 3-pentenyl, 4-pentenyl, dimethylallyl, 1-hexenyl, 3-hexenyl, 5-hexenyl, 1-heptenyl, 3-heptenyl, 6-heptenyl, and 7-octenyl groups;
15 exemplary alkoxyalkyl groups include methoxymethyl, ethoxymethyl, propoxymethyl, butoxymethyl, pentoxymethyl, hexyloxymethyl, heptyloxymethyl, methoxyethyl, ethoxyethyl, propoxyethyl, butoxyethyl, pentoxyethyl, hexyloxyethyl, methoxypropyl, ethoxypropyl, propoxypropyl,
20 butoxypropyl, methoxybutyl, ethoxybutyl, propoxybutyl, methoxypentyl, ethoxypentyl, methoxyhexyl, and methoxyheptyl groups.

Examples of the normal or branched alkyl groups of 1 to 4 carbon atoms which may be further substituted include
25 methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl and tert-butyl groups; examples of the alkoxy groups include methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, and tert-butoxy groups; examples of phenyl group (which may be replaced by alkyl or alkoxy groups of 1 to 4 carbon
30 atoms, nitro groups or acetyl groups) include phenyl, tryl, p-tert-butoxyphenyl, p-acetylphenyl and p-nitrophenyl groups; and examples of the heteroaromatic group of 3 to 5 carbon atoms include pyridyl and furyl groups.

35 Illustrative examples are:

onium salts such as diphenyliodonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)phenyliodonium

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trifluoromethanesulfonate, diphenyliodonium p-toluenesulfonate, (p-tert-butoxyphenyl)phenyliodonium p-toluenesulfonate, triphenylsulfonium trifluoromethanesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium

5 trifluoromethanesulfonate, bis(p-tert-butoxyphenyl)phenylsulfonium trifluoromethanesulfonate, tris(p-tert-butoxyphenyl)sulfonium trifluoromethanesulfonate, triphenylsulfonium p-toluenesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium p-toluenesulfonate, bis(p-tert-butoxyphenyl)phenylsulfonium p-toluenesulfonate,

10 tris(p-tert-butoxyphenyl)sulfonium p-toluenesulfonate, triphenylsulfonium nonafluorobutanesulfonate, triphenylsulfonium butanesulfonate, trimethylsulfonium trifluoromethanesulfonate, trimethylsulfonium p-toluenesulfonate,

15 cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium p-toluenesulfonate, dimethylphenylsulfonium trifluoromethanesulfonate, dimethylphenylsulfonium p-toluenesulfonate,

20 dicyclohexylphenylsulfonium trifluoromethanesulfonate, dicyclohexylphenylsulfonium p-toluenesulfonate, trinaphthylsulfonium trifluoromethanesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, (2-norbornyl)methyl(2-

25 oxocyclohexyl)sulfonium trifluoromethanesulfonate, ethylene-bis[methyl(2-oxocyclopentyl)sulfonium trifluoromethanesulfonate], and 1,2'-naphthylcarbonylmethyl-tetrahydrothiophenium triflate;

diazomethane derivatives such as

30 bis(benzenesulfonyl)diazomethane, bis(p-toluenesulfonyl)-diazomethane, bis(xylenesulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(cyclopentylsulfonyl)diazomethane, bis(n-butylsulfonyl)diazomethane, bis(isobutylsulfonyl)-

35 diazomethane, bis(sec-butylsulfonyl)diazomethane, bis(n-propylsulfonyl)diazomethane, bis(isopropylsulfonyl)-diazomethane, bis(tert-butylsulfonyl)diazomethane, bis(n-

amylsulfonyl)diazomethane, bis(isoamylsulfonyl)-
diazomethane, bis(sec-amylsulfonyl)diazomethane, bis(tert-
amylsulfonyl)diazomethane, 1-cyclohexylsulfonyl-1-(tert-
butylsulfonyl)diazomethane, 1-cyclohexylsulfonyl-1-(tert-
5 amylsulfonyl)diazomethane, and 1-tert-amylsulfonyl-1-
(tert-butylsulfonyl)diazomethane;

glyoxime derivatives such as bis-o-(p-
toluenesulfonyl)- α -dimethylglyoxime, bis-o-(p-
toluenesulfonyl)- α -diphenylglyoxime, bis-o-(p-
10 toluenesulfonyl)- α -dicyclohexylglyoxime, bis-o-(p-
toluenesulfonyl)-2,3-pentanedione-glyoxime, bis-o-(p-
toluenesulfonyl)-2-methyl-3,4-pentanedione-glyoxime, bis-o-
(n-butanesulfonyl)- α -dimethylglyoxime, bis-o-(n-butane-
sulfonyl)- α -diphenylglyoxime, bis-o-(n-butanesulfonyl)- α -
15 dicyclohexylglyoxime, bis-o-(n-butanesulfonyl)-2,3-
pentanedione-glyoxime, bis-o-(n-butanesulfonyl)-2-methyl-
3,4-pentanedione-glyoxime, bis-o-(methanesulfonyl)- α -
dimethylglyoxime, bis-o-(trifluoromethanesulfonyl)- α -
dimethylglyoxime, bis-o-(1,1,1-trifluoroethanesulfonyl)- α -
20 dimethylglyoxime, bis-o-(tert-butanesulfonyl)- α -
dimethylglyoxime, bis-o-(perfluorooctanesulfonyl)- α -
dimethylglyoxime, bis-o-(cyclohexanesulfonyl)- α -
dimethylglyoxime, bis-o-(benzenesulfonyl)- α -
dimethylglyoxime, bis-o-(p-fluorobenzenesulfonyl)- α -
25 dimethylglyoxime, bis-o-(p-tert-butylbenzenesulfonyl)- α -
dimethylglyoxime, bis-o-(xylenesulfonyl)- α -
dimethylglyoxime, and bis-o-(camphorsulfonyl)- α -dimethyl-
glyoxime;

bissulfone derivatives such as bis(naphthylsulfonyl)-
30 methane, bis(trifluoromethylsulfonyl)methane,
bis(methylsulfonyl)methane, bis(ethylsulfonyl)methane,
bis(propylsulfonyl)methane, bis(isopropylsulfonyl)methane,

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bis(p-toluenesulfonyl)methane, and bis(benzenesulfonyl)-methane;

5 β -ketosulfone derivatives such as 2-cyclohexylcarbonyl-2-(p-toluenesulfonyl)propane and 2-isopropylcarbonyl-2-(p-toluenesulfonyl)propane;

disulfone derivatives such as diphenyl disulfone and dicyclohexyl disulfone;

10 nitrobenzyl sulfonate derivatives such as 2,6-dinitrobenzyl p-toluenesulfonate and 2,4-dinitrobenzyl p-toluenesulfonate;

sulfonate ester derivatives such as 1,2,3-tris(methanesulfonyloxy)benzene, 1,2,3-tris(trifluoromethanesulfonyloxy)benzene, and 1,2,3-tris(p-toluenesulfonyloxy)benzene; and

15 sulfonic acid ester derivatives of N-hydroxyimide compounds such as N-hydroxysuccinimide methylsulfonate, N-hydroxysuccinimide trifluoromethylsulfonate, N-hydroxysuccinimide ethylsulfonate, N-hydroxysuccinimide propylsulfonate, N-hydroxysuccinimide isopropylsulfonate, N-hydroxysuccinimide pentylsulfonate, N-hydroxysuccinimide octylsulfonate, N-hydroxysuccinimide p-toluenesulfonate, N-hydroxysuccinimide p-anisylsulfonate, N-hydroxysuccinimide 2-chloroethylsulfonate, N-hydroxysuccinimide benzenesulfonate, N-hydroxysuccinimide 25 2,4,6-trimethylphenylsulfonate, N-hydroxysuccinimide naphthylsulfonate, N-hydroxy-2-phenylsuccinimide methylsulfonate, N-hydroxymaleimide methylsulfonate, N-hydroxymaleimide ethylsulfonate, N-hydroxy-2-phenylmaleimide methylsulfonate, N-hydroxyglutarimide 30 methylsulfonate, N-hydroxyglutarimide phenylsulfonate, N-hydroxyphthalimide methylsulfonate, N-hydroxyphthalimide phenylsulfonate, N-hydroxyphthalimide trifluoromethanesulfonate, N-hydroxyphthalimide p-toluenesulfonate, N-hydroxy-1,8-naphthalimide methylsulfonate, N-hydroxy-1,8-naphthalimide phenylsulfonate, N-hydroxy-5-norbornene-2,3-dicarboxyimide methylsulfonate, N-hydroxy-5-norbornene-2,3-dicarboxyimide trifluoromethanesulfonate,

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and N-hydroxy-5-norbornene-2,3-dicarboxyimide p-toluene-sulfonate.

Preferred among these are onium salts such as triphenylsulfonium trifluoromethanesulfonate, (p-tert-
5 butoxyphenyl)diphenylsulfonium trifluoromethanesulfonate, tris(p-tert-butoxyphenyl)sulfonium trifluoromethane-sulfonate, triphenylsulfonium p-toluenesulfonate, (p-tert-butoxyphenyl)diphenylsulfonium p-toluenesulfonate, tris(p-tert-butoxyphenyl)sulfonium p-toluenesulfonate,
10 trinaphthylsulfonium trifluoromethanesulfonate, cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, (2-norbornyl)methyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, and 1,2'-naphthylcarbonylmethyltetrahydrothiophenium triflate;
15 diazomethane derivatives such as bis(benzenesulfonyl)-diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(n-butylsulfonyl)diazomethane, bis(isobutylsulfonyl)-diazomethane, bis(sec-butylsulfonyl)diazomethane, bis(n-propylsulfonyl)diazomethane, bis(isopropylsulfonyl)-
20 diazomethane, and bis(tert-butylsulfonyl)diazomethane; glyoxime derivatives such as bis-o-(p-toluenesulfonyl)- α -dimethylglyoxime and bis-o-(n-butan sulfonyl)- α -dimethylglyoxime; bissulfone derivatives such as bisnaphthyl-sulfonylmethane; and sulfonic acid ester derivatives of N-hydroxyimide compounds such as N-hydroxysuccinimide methylsulfonate, N-hydroxysuccinimide trifluoromethyl-sulfonate, N-hydroxysuccinimide propylsulfonate, N-hydroxysuccinimide isopropylsulfonate, N-
25 hydroxysuccinimide pentylsulfonate, N-hydroxysuccinimide p-toluenesulfonate, N-hydroxy-1,8-naphthalimide methylsulfonate, N-hydroxy-1,8-naphthalimide phenylsulfonate, and N-hydroxysuccinimide trifluoromethanesulfonate. It is noted that the photoacid
30 generators mentioned above may be used alone or in admixture of two or more. The onium salts are effective for improving rectangularity while the diazomethane.

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derivatives and glyoxime derivatives are effective for reducing standing wave. A combination of an onium salt with a diazomethane or glyoxime derivative allows for finer profile adjustment.

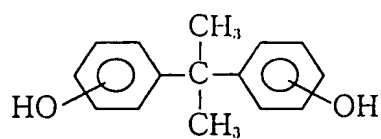
5 Desirably, the photoacid generator is added in an amount of 0.1 to 15 parts, especially 0.5 to 8 parts per 100 parts of the base resin. Sensitivity would be low with less than 0.1 part of the photoacid generator. More than 15 parts of the photoacid generator would lower an
10 alkali dissolution rate to detract from resolution. Additionally heat resistance may lower because monomeric components become excessive.

In the resist composition of the invention, a dissolution inhibitor may be blended as component (D).
15 The dissolution inhibitor blended herein is a compound with an average molecular weight of 100 to 1,000, preferably 150 to 800 and having at least two phenolic hydroxyl groups in a molecule wherein the hydrogen atom of the phenolic hydroxyl group is replaced by an acid labile
20 group in an average proportion of 0 mol% to 100 mol% of the entire phenolic hydroxyl groups, or a compound with an average molecular weight of 100 to 1,000, preferably 150 to 800 and having a carboxyl group in a molecule wherein the hydrogen atom of the carboxyl group is replaced by an
25 acid labile group in an average proportion of 80 mol% to 100 mol% of the entire carboxyl groups.

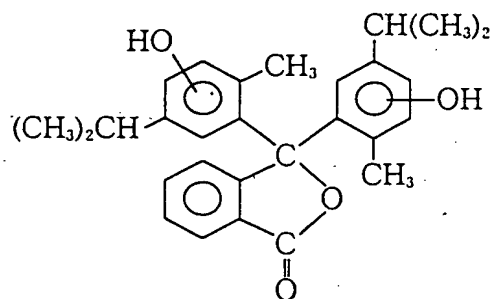
The percent average replacement of the hydrogen atom of phenolic hydroxyl group or carboxyl group by an acid labile group is at least 0 mol%, preferably at least 30
30 mol% of the entire phenolic hydroxyl groups or carboxyl groups, with the upper limit being 100 mol%, more preferably 80 mol%.

The compounds having at least two phenolic hydroxyl groups or the compounds having a carboxyl group are
35 preferably compounds of the following formulae (i) to (xiv):

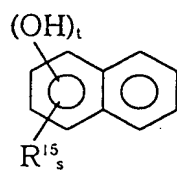
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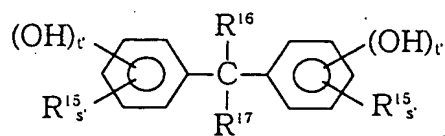
(i)



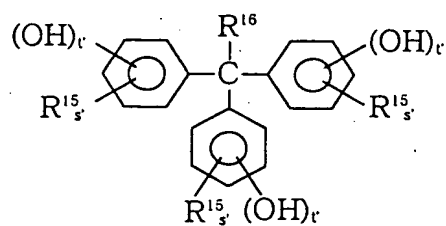
(ii)



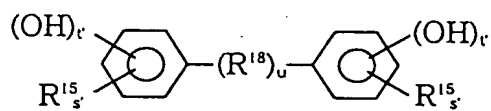
(iii)



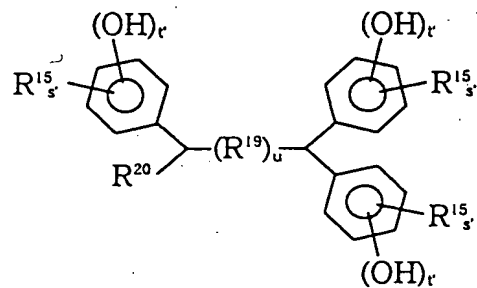
(iv)



(v)



(vi)



(vii)

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(viii)



(ix)



(x)



(xi)



(xj̄i)



(xiii)



In the formulae, R^{15} and R^{16} are independently a hydrogen atom or normal or branched alkyl or alkenyl group having 1 to 8 carbon atoms. R^{17} is a hydrogen atom, normal or branched alkyl or alkenyl group having 1 to 8 carbon atoms, or $-(R^{21})_h-COOH$. R^{18} is a group $-(CH_2)_i-$ wherein i is 2 to 10, arylene group having 6 to 10 carbon atoms, carbonyl group, sulfonyl group, oxygen atom or sulfur atom. R^{19} is an alkylene group having 1 to 10 carbon atoms, arylene group having 6 to 10 carbon atoms, carbonyl group, sulfonyl group, oxygen atom or sulfur atom. R^{20} is a hydrogen atom, normal or branched alkyl group having 1 to 8 carbon atoms, alkenyl group, hydroxyl-substituted phenyl group or hydroxyl-substituted naphthyl group. R^{21} is a normal or branched alkylene group having 1 to 10 carbon atoms. R^{22} is a hydrogen atom or hydroxyl group. Letter j is an integer of 0 to 5, u and h each are 0 or 1, and s , t , s' , t' , s'' , and t'' are numbers satisfying $s + t = 8$, $s' + t' = 5$, and $s'' + t'' = 4$ such that at least one hydroxyl group is attached to each phenyl skeleton. α is such a number that the compound of formula (viii) or (ix) may have a molecular weight of 100 to 1,000.

Exemplary groups represented by R¹⁵ and R¹⁶ are hydrogen, methyl, ethyl, butyl, propyl, ethynyl, and cyclohexyl groups. Exemplary groups represented by R¹⁷ are as exemplified for R¹⁵ and R¹⁶ as well as -COOH and -CH₂COOH. Exemplary groups represented by R¹⁸ are ethylene, phenylene, carbonyl, and sulfonyl groups, oxygen and sulfur atoms. Exemplary groups represented by R¹⁹ are methylene and as exemplified for R¹⁸. Exemplary groups represented by R²⁰ are hydrogen, methyl, ethyl, butyl, propyl, ethynyl, cyclohexyl, and hydroxyl-substituted phenyl and naphthyl groups.

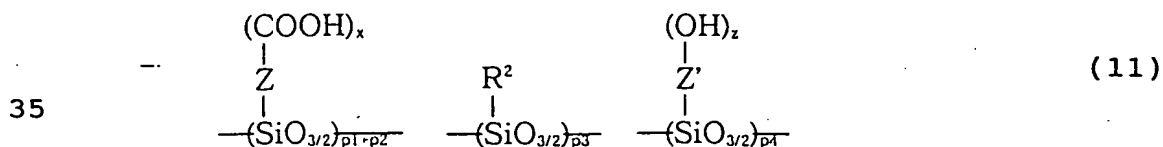
The acid labile group in the dissolution inhibitor includes groups of the general formulae (4) and (5), tert-alkyl groups of 4 to 20 carbon atoms, trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms, and
5 oxoalkyl groups of 4 to 20 carbon atoms.

The dissolution inhibitors are blended in the resist composition in an amount of 0 to 50 parts, preferably 5 to 50 parts, more preferably 10 to 30 parts per 100 parts of
10 the base resin while they may be used alone or in admixture of two or more. Less than 5 parts of the dissolution inhibitor would be ineffective for improving resolution whereas more than 50 parts would induce pattern thinning and detract from resolution.

The dissolution inhibitor mentioned above can be
15 synthesized by chemically reacting an acid labile group with a compound having a phenolic hydroxyl group or carboxyl group as in the preparation of the base resin.

In addition to or instead of the dissolution
inhibitor described above, there may be blended as another
20 dissolution inhibitor a compound having a weight average molecular weight of less than 1,000 and a carboxyl group in a molecule wherein the hydrogen atom of the carboxyl group is partially replaced by an acid labile group in an average proportion of 0% to 100% of the entire carboxyl
25 groups.

The compound in which the hydrogen atom of a carboxyl group is partially replaced by an acid labile group is preferably at least one member selected from compounds comprising recurring units of the following general
30 formula (11) and having a weight average molecular weight of less than 1,000.



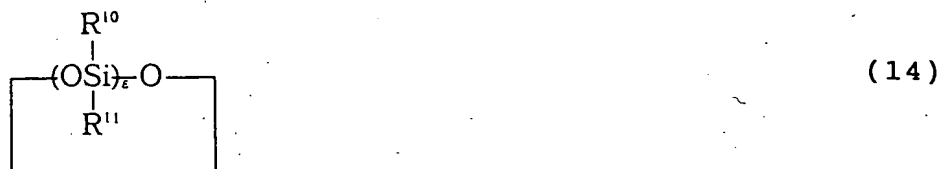
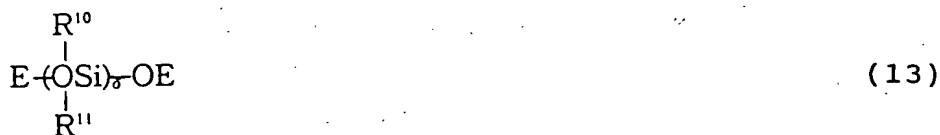
In the formula, Z, Z', R², p1, p2, p3, p4, x and z are as defined above.

The acid labile group in the above-mentioned dissolution inhibitor includes groups of the general formulae (4) and (5), tert-alkyl groups of 4 to 20 carbon atoms, trialkylsilyl groups whose alkyl groups each have 1 to 6 carbon atoms, and oxoalkyl groups of 4 to 20 carbon atoms.

The blending amount of the other dissolution inhibitor is preferably such that the combined amount with the first-mentioned dissolution inhibitor is 0 to 50 parts, more preferably 0 to 30 parts, especially 0 to 5 parts per 100 parts of the base resin.

The other dissolution inhibitor can be synthesized by chemically reacting an acid labile group with a compound having a carboxyl group as in the preparation of the base resin.

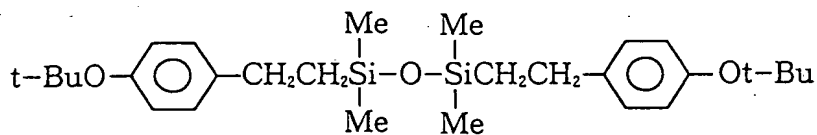
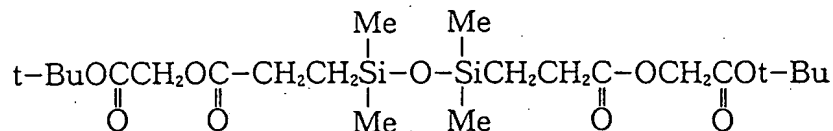
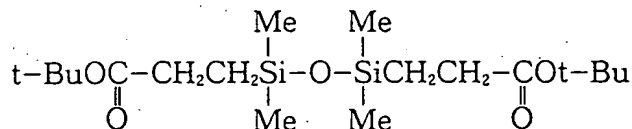
A silicone compound is also useful as the dissolution inhibitor (D) because it does not adversely affect oxygen plasma etching resistance. The silicone compound dissolution inhibitors which can be used herein are preferably silicone compounds of the following general formulae (12) to (14) wherein carboxyl groups or hydroxyl groups are protected with tert-butyl or tert-butoxycarbonylmethyl groups.



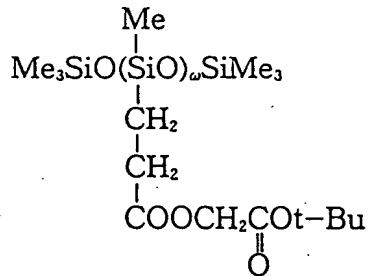
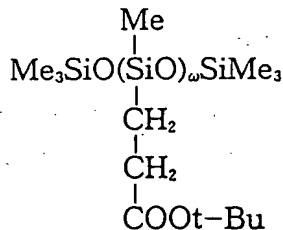
In the formulae, R^{10} is a methyl or phenyl group. R^{11} is a carboxyethyl or p-hydroxyphenylalkyl group (wherein the alkyl groups are normal, branched or cyclic alkyl groups of 1 to 8 carbon atoms). E is a trimethylsilyl, triphenylsilyl or $-\text{SiR}^{10}\text{R}^{11}$ group wherein R^{10} and R^{11} are as defined above. Letter γ is an integer of 0 to 50, δ is an integer of 1 to 50, and ϵ is an integer of 3 to 10.

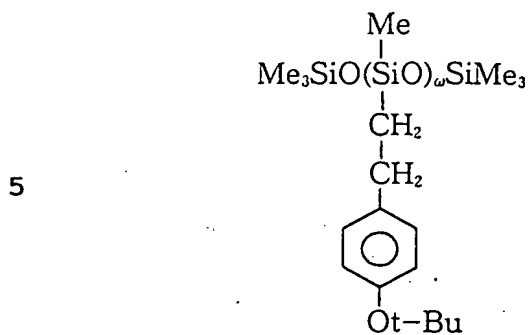
The silicone compounds obtained by protecting the carboxyl or hydroxyl groups of the silicone compounds of formulae (12) to (14) with alkali-soluble groups (e.g., tert-butyl or tert-butoxycarbonylmethyl groups) are exemplified by groups of the following classes A to C. Me is methyl and t-Bu is tert-butyl.

Class A



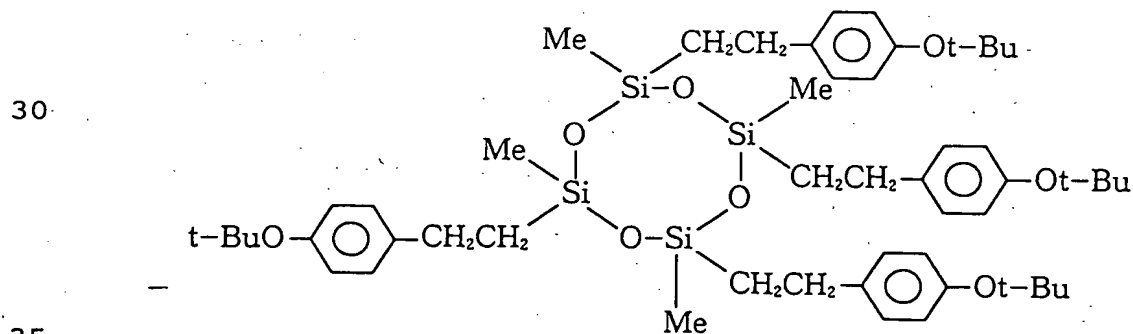
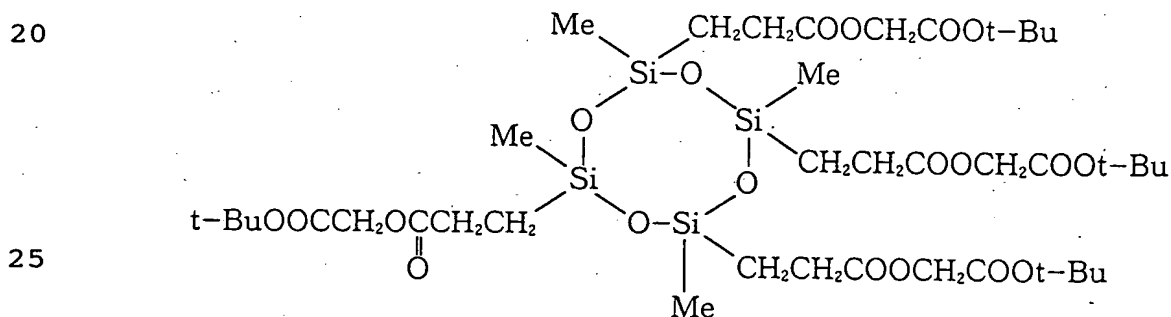
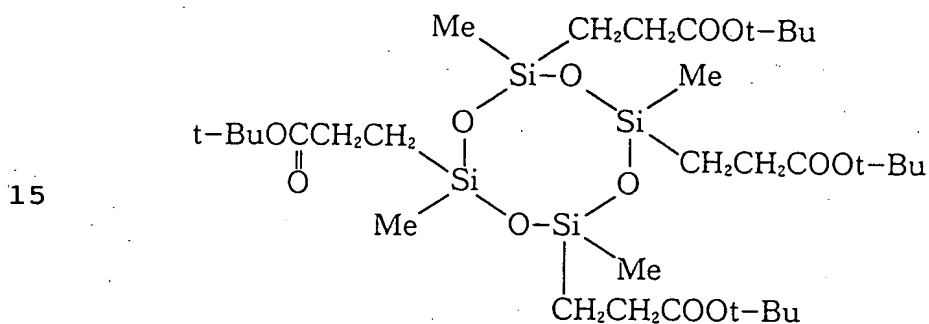
Class B





ω is 1 to 50.

10 Class C



The amount of the dissolution inhibitor blended is preferably up to 40% by weight, more preferably 10 to 30%

by weight based on the entire base resin. More than 40% by weight of the dissolution inhibitor would cause a marked decline of the oxygen plasma etching resistance of resist film to such an extent that the composition might not be applicable as the two-layer resist.

In the resist composition of the invention, a basic compound may be blended as component (E).

The basic compound blended as component (E) is preferably a compound which can suppress the diffusion rate at which the acid generated from the photoacid generator diffuses into a resist coating. The blending of such a basic compound suppresses the diffusion rate of acid in a resist coating to improve resolution, suppresses a change of sensitivity after exposure, and mitigates substrate and environment dependency, achieving improvements in exposure latitude and pattern profile.

Included in the basic compound are primary, secondary and tertiary aliphatic amines, hybrid amines, aromatic amines, heterocyclic amines, carboxyl-bearing nitrogenous compounds, sulfonyl-bearing nitrogenous compounds, hydroxyl-bearing nitrogenous compounds, hydroxyphenyl-bearing nitrogenous compounds, alcoholic nitrogenous compounds, amide derivatives, and imide derivatives.

Examples of the primary aliphatic amine include ammonia, methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, iso-butylamine, sec-butylamine, tert-butylamine, pentylamine, tert-amylamine, cyclopentylamine, hexylamine, cyclohexylamine, heptylamine, octylamine, nonylamine, decylamine, dodecylamine, cetylamine, methylenediamine, ethylenediamine, and tetraethylenepentamine. Examples of the secondary aliphatic amine include dimethylamine, diethylamine, di-n-propylamine, di-iso-propylamine, di-n-butylamine, di-iso-butylamine, di-sec-butylamine, dipentylamine, dicyclopentylamine, dihexylamine, dicyclohexylamine, diheptylamine, dioctylamine, dinonylamine, didecylamine, didodecylamine, dicetylamine, N,N-dimethyl-

methylenediamine, N,N-dimethylethylenediamine, and N,N-dimethyltetraethylenepentamine. Examples of the tertiary aliphatic amine include trimethylamine, triethylamine, tri-n-propylamine, tri-iso-propylamine, tri-n-butylamine, tri-iso-butylamine, tri-sec-butylamine, tripentylamine, tricyclopentylamine, trihexylamine, tricyclohexylamine, triheptylamine, trioctylamine, trinonylamine, tridecylamine, tridodecylamine, tricetylamine, N,N,N',N'-tetramethylmethylenediamine, N,N,N',N'-tetramethylethylenediamine, and N,N,N',N'-tetramethyltetraethylenepentamine.

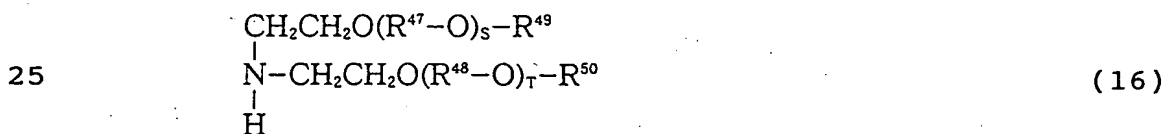
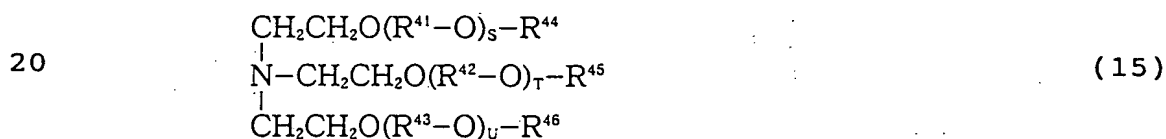
Examples of the hybrid amine include dimethylethylamine, methylethylpropylamine, benzylamine, phenethylamine, and benzyldimethylamine. Examples of the aromatic and heterocyclic amines include aniline derivatives (e.g., aniline, N-methylaniline, N-ethylamine, N-propylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, ethylaniline, propylaniline, trimethylaniline, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline, 2,6-dinitroaniline, 3,5-dinitroaniline, and N,N-dimethyltoluidine), diphenyl(p-tolyl)amine, methyldiphenylamine, triphenylamine, phenylenediamine, naphthylamine, diaminonaphthalene, pyrrole derivatives (e.g., pyrrole, 2H-pyrrole, 1-methylpyrrole, 2,4-dimethylpyrrole, 2,5-dimethylpyrrole, and N-methylpyrrole), oxazole derivatives (e.g., oxazole and isooxazole), thiazole derivatives (e.g., thiazole and isothiazole), imidazole derivatives (e.g., imidazole, 4-methylimidazole, and 4-methyl-2-phenylimidazole), pyrazole derivatives, furazane derivatives, pyrroline derivatives (e.g., pyrroline and 2-methyl-1-pyrroline), pyrrolidine derivatives (e.g., pyrrolidine, N-methylpyrrolidine, pyrrolidinone, and N-methylpyrrolidone), imidazoline derivatives, imidazolidine derivatives, pyridine derivatives (e.g., pyridine, methylpyridine, ethylpyridine, propylpyridine, butylpyridine, 4-(1-

5 dimethoxyypyridine, 1-methyl-2-pyridone, 4-pyrrolidino-
pyridine, 1-methyl-4-phenylpyridine, 2-(1-ethylpropyl)-
pyridine, aminopyridine, and dimethylaminopyridine),
pyridazine derivatives, pyrimidine derivatives, pyrazine
derivatives, pyrazoline derivatives, pyrazolidine
0 derivatives, piperidine derivatives, piperazine
derivatives, morpholine derivatives, indole derivatives,
isoindole derivatives, 1H-indazole derivatives, indoline
derivatives, quinoline derivatives (e.g., quinoline and 3-
quinolinecarbonitrile), isoquinoline derivatives,
5 cinnoline derivatives, quinazoline derivatives,
quinoxaline derivatives, phthalazine derivatives, purine
derivatives, pteridine derivatives, carbazole derivatives,
phenanthridine derivatives, acridine derivatives,
phenazine derivatives, 1,10-phenanthroline derivatives,
10 adenine derivatives, adenosine derivatives, guanine
derivatives, guanosine derivatives, uracil derivatives,
and uridine derivatives.

30 sulfonyl-bearing nitrogenous compound include 3-
pyridinesulfonic acid and pyridinium p-toluenesulfonate.
Examples of the hydroxyl-bearing nitrogenous compound,
hydroxyphenyl-bearing nitrogenous compound, and alcoholic
nitrogenous compound include 2-hydroxypyridine,
35 aminocresole, 2,4-quinoline diol, 3-indolemethanol
hydrate, monoethanolamine, diethanolamine,
triethanolamine, N-ethyldiethanolamine, N,N-diethyl-

ethanolamine, triisopropanolamine, 2,2'-iminodiethanol, 2-aminoethanol, 3-amino-1-propanol, 4-amino-1-butanol, 4-(2-hydroxyethyl)morpholine, 2-(2-hydroxyethyl)pyridine, 1-(2-hydroxyethyl)piperazine, 1-[2-(2-hydroxyethoxy)ethyl]-
 5 piperazine, piperidine ethanol, 1-(2-hydroxyethyl)-pyrrolidine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 3-piperidino-1,2-propane diol, 3-pyrrolidino-1,2-propane diol, 8-hydroxyjulolidine, 3-quinuclidinol, 3-tropanol, 1-methyl-2-pyrrolidine ethanol, 1-aziridine ethanol, N-(2-
 10 hydroxyethyl)phthalimide, and N-(2-hydroxyethyl)-isonicotinamide. Examples of the amide derivative include formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionamide, and benzamide. Exemplary imide derivatives
 15 are phthalimide, succinimide, and maleimide.

Further, basic compounds of the following general formulae (15) and (16) may also be blended.



In the formulae, R^{41} , R^{42} , R^{43} , R^{47} , and R^{48} are independently normal, branched or cyclic alkylene groups
 30 of 1 to 20 carbon atoms. R^{44} , R^{45} , R^{46} , R^{49} , and R^{50} are independently hydrogen, alkyl groups of 1 to 20 carbon atoms, or amino groups. Alternatively, R^{44} and R^{45} , R^{45} and R^{46} , R^{44} and R^{46} , or R^{44} and R^{45} and R^{46} , and R^{49} and R^{50} , taken together, may form a ring. S, T and U are integers of 0
 35 to 20, with the proviso that hydrogen is excluded from R^{44} , R^{45} , R^{46} , R^{49} , and R^{50} when S, T and U are equal to 0.

The alkylene groups represented by R^{41} , R^{42} , R^{43} , R^{47} , and R^{48} are preferably those of 1 to 20 carbon atoms, more preferably 1 to 10 carbon atoms, most preferably 1 to 8 carbon atoms, such as methylene, ethylene, n-propylene, isopropylene, n-butylene, isobutylene, n-pentylene, isopentylene, hexylene, nonylene, decylene, cyclopentylene, and cyclohexylene.

The alkyl groups represented by R^{44} , R^{45} , R^{46} , R^{49} , and R^{50} are preferably those of 1 to 20 carbon atoms, more preferably 1 to 8 carbon atoms, most preferably 1 to 6 carbon atoms, while they may be normal, branched or cyclic. Exemplary alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, hexyl, nonyl, decyl, dodecyl, tridecyl, cyclopentyl, and cyclohexyl.

Where R^{44} and R^{45} , R^{45} and R^{46} , R^{44} and R^{46} , R^{44} and R^{45} and R^{46} , or R^{49} and R^{50} form a ring, they each preferably have an alkylene group having 1 to 20 carbon atoms, more preferably 1 to 8 carbon atoms, most preferably 1 to 6 carbon atoms and the ring may have branched therefrom an alkyl group of 1 to 6 carbon atoms, especially 1 to 4 carbon atoms.

Each of S, T and U is an integer of 0 to 20, preferably 1 to 10, more preferably 1 to 8.

Illustrative examples of the compounds of formulae (15) and (16) include tris{2-(methoxymethoxy)ethyl}amine, tris{2-(methoxyethoxy)ethyl}amine, tris[2-((2-methoxyethoxy)methoxy)ethyl]amine, tris{2-(2-methoxyethoxy)ethyl}amine, tris{2-(1-methoxyethoxy)ethyl}amine, tris{2-(1-ethoxyethoxy)ethyl}amine, tris{2-(1-ethoxypropoxy)ethyl}amine, tris[2-((2-hydroxyethoxy)ethoxy)ethyl]amine, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane, 1,4,10,13-tetraoxa-7,16-diazabicyclooctadecane, 1-aza-12-crown-4, 1-aza-15-crown-5, and 1-aza-18-crown-6. Especially preferred basic compounds are tertiary amines, aniline

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FOUO 90 02 28 86

derivatives, pyrrolidine derivatives, pyridine derivatives, quinoline derivatives, amic acid derivatives, nitrogenous compounds having a hydroxyl group, nitrogenous compounds having a hydroxyphenyl group, alcoholic

- 5 nitrogenous compounds, amide derivatives, imide derivatives, tris{2-(methoxymethoxy)ethyl}amine, tris{2-(2-methoxyethoxy)ethyl}amine, tris[2-((2-methoxyethoxy)-methyl)ethyl]amine, and 1-aza-15-crown-5.

10 Preferably the basic compound is blended in an amount of 0.001 to 10 parts, especially about 0.01 to 1 part per part of the photoacid generator. An addition amount of less than 0.001 part would fail to provide an additive effect whereas more than 10 parts would adversely affect resolution and sensitivity.

- 15 In the resist composition of the invention, a compound having a group represented by $\equiv\text{C}-\text{COOH}$ in a molecule may be blended as component (F).

The compound having a group $\equiv\text{C}-\text{COOH}$ in a molecule blended as component (F) may be at least one compound
20 selected from the following classes I and II although the invention is not limited thereto. Blending of component (F) is effective for improving the PED stability of resist and improving the edge roughness of resist on nitride film substrates.

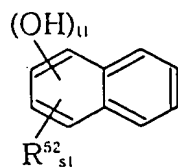
25 Class I

Compounds of the following general formulae (17) to (26) wherein some or all of the hydrogen atoms of phenolic hydroxyl groups are replaced by $-\text{R}^{51}-\text{COOH}$ wherein R^{51} is a normal or branched alkylene group having 1 to 10 carbon
30 atoms and the molar fraction of the phenolic hydroxyl group (C mol) in the molecule to the group $\equiv\text{C}-\text{COOH}$ (D mol) is $\text{C}/(\text{C} + \text{D}) = 0.1$ to 1.0.

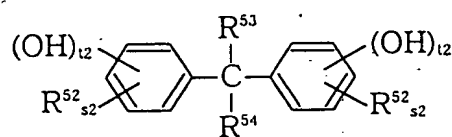
Class II

Compounds of the following general formulae (27) to
35 (31)

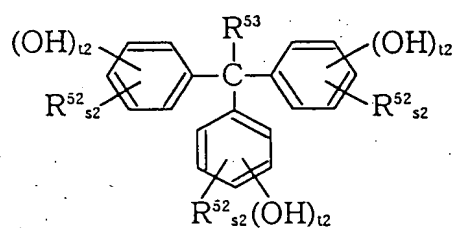
Class I



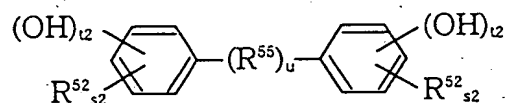
(17)



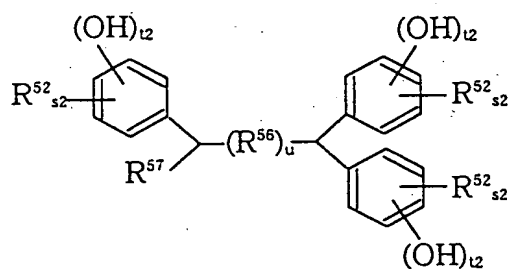
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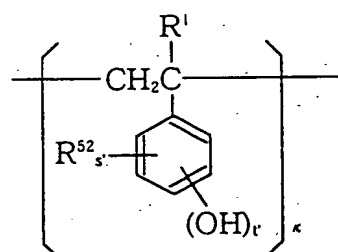
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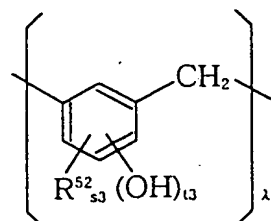
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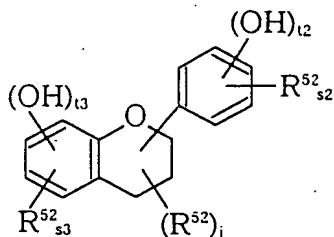
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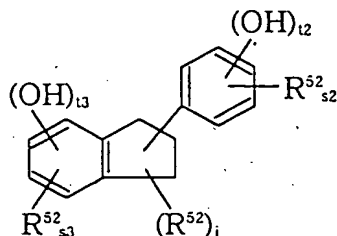
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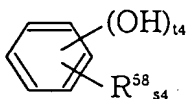
(23)



(24)



(25)

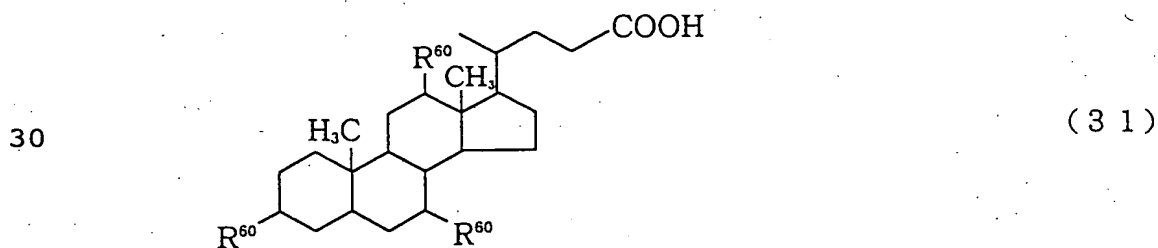
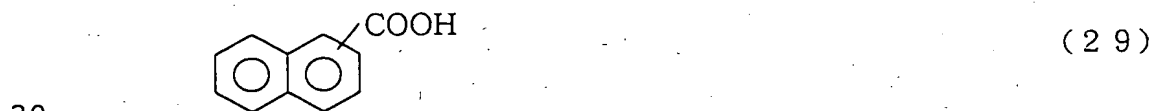
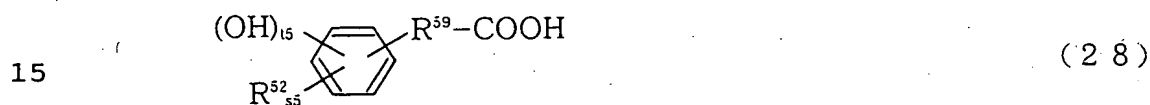
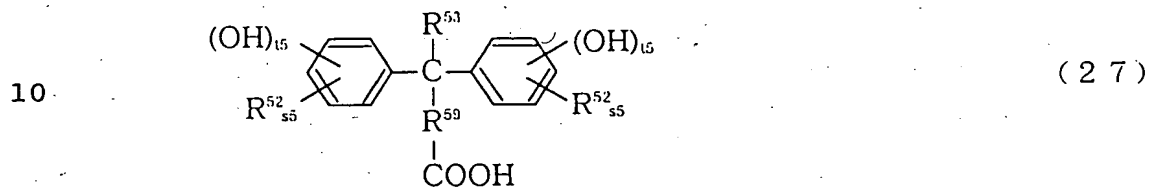


(26)

In the formulae, R^1 is a hydrogen atom or methyl group. R^{52} and R^{53} are independently a hydrogen atom or normal or branched alkyl or alkenyl group having 1 to 8 carbon atoms. R^{54} is a hydrogen atom, normal or branched alkyl or alkenyl group having 1 to 8 carbon atoms, or $-(R^{59})_h-COOR'$ wherein R' is a hydrogen atom or $-R^{59}-COOH$. R^{55} is a group $-(CH_2)_i-$ wherein i is 2 to 10, arylene group having 6 to 10 carbon atoms, carbonyl group, sulfonyl group, oxygen atom or sulfur atom. R^{56} is an alkylene group having 1 to 10 carbon atoms, arylene group having 6 to 10 carbon atoms, carbonyl group, sulfonyl group, oxygen atom or sulfur atom. R^{57} is a hydrogen atom, normal or branched alkyl group having 1 to 8 carbon atoms, alkenyl group, hydroxyl-substituted phenyl group or hydroxyl-substituted naphthyl group. R^{58} is a hydrogen atom, normal or branched alkyl or alkenyl group having 1 to 8 carbon atoms, or $-R^{59}-COOH$. R^{59} is a normal or branched alkylene group having 1 to 10 carbon atoms. Letter j is an integer of 0 to 5, u and h each are 0 or 1, and s_1 , t_1 , s_2 , t_2 , s_3 , t_3 , s_4 , and t_4 are numbers satisfying $s_1 + t_1 = 8$, $s_2 + t_2 = 5$, $s_3 + t_3 = 4$, and $s_4 + t_4 = 6$ such that at least

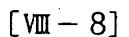
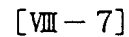
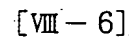
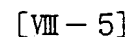
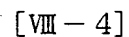
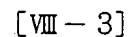
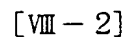
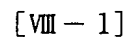
one hydroxyl group is attached to each phenyl skeleton. κ is such a number that the compound of formula (23) may have a weight average molecular weight of 1,000 to 5,000. λ is such a number that the compound of formula (24) may have a weight average molecular weight of 1,000 to 10,000.

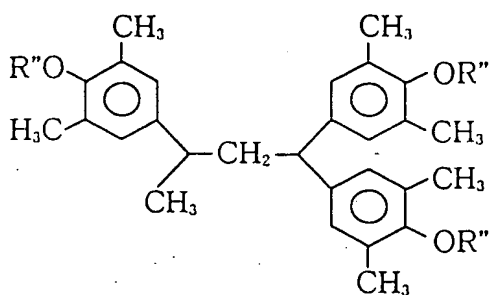
Class II



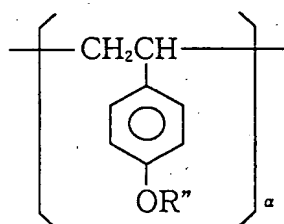
In the formulae, R^{52} , R^{53} , and R^{59} are as defined above, and s_5 and t_5 are numbers satisfying $s_5 \geq 0$, $t_5 \geq 0$, and $s_5 + t_5 = 5$. R^{60} is hydrogen or a hydroxyl group, and h' is equal to 0 or 1.

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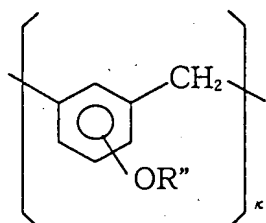




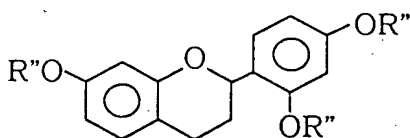
[VIII - 9]



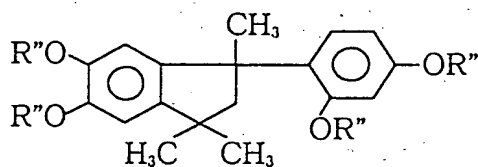
[VIII - 10]



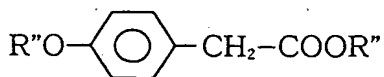
[VIII - 11]



[VIII - 12]

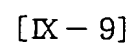
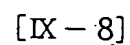
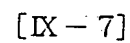
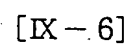
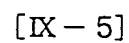
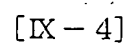
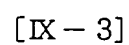
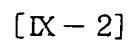
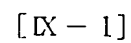


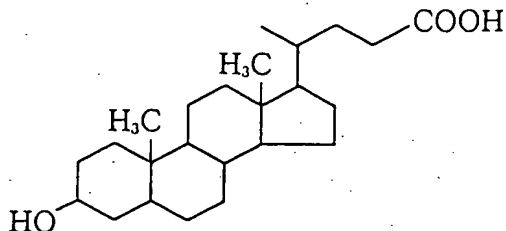
[VIII - 13]



[VIII - 14]

R'' is a hydrogen atom or a group CH₂COOH. In each compound, 10 to 100 mol% of R'' is CH₂COOH. Letters α and κ are as defined above.





[IX-10]

5

The compounds having a group $\equiv\text{C}-\text{COOH}$ in a molecule may be used alone or in admixture of two or more.

The compound having a group $\equiv\text{C}-\text{COOH}$ in a molecule is blended in the resist composition in an amount of 0 to 5 parts, preferably 0.1 to 5 parts, more preferably 0.1 to 3 parts, most preferably 0.1 to 2 parts per 100 parts of the base resin. More than 5 parts of the compound would adversely affect the resolution of the resist composition.

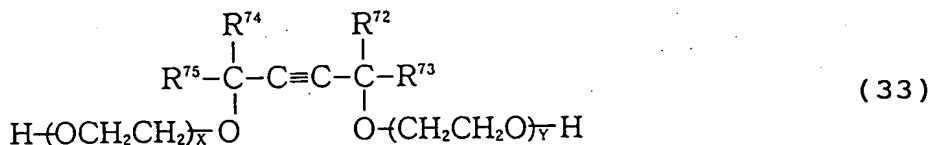
In the resist composition of the invention, an acetylene alcohol derivative may be blended as component (G) for thereby improving shelf stability.

The acetylene alcohol derivative used herein is preferably selected from compounds of the following general formulae (32) and (33).

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30

In the formulae, R^{71} , R^{72} , R^{73} , R^{74} , and R^{75} each are hydrogen or a normal, branched or cyclic alkyl group having 1 to 8 carbon atoms, X and Y are 0 or positive numbers satisfying $0 \leq X \leq 30$, $0 \leq Y \leq 30$, and $0 \leq X + Y \leq 40$.

35

Useful acetylene alcohol derivatives are commercially available under the trade name of Surfynol 61, Surfynol 82, Surfynol 104, Surfynol 104E, Surfynol 104H, Surfynol

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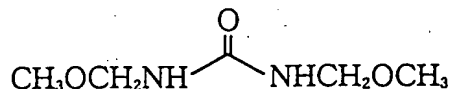
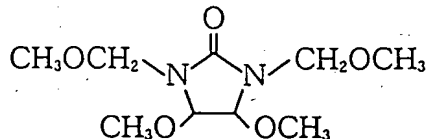
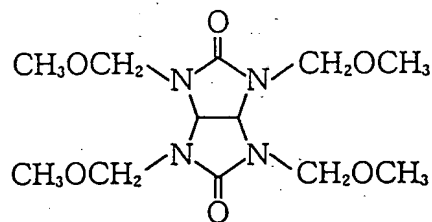
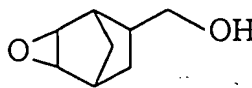
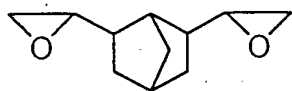
104A, Surfynol TG, Surfynol PC, Surfynol 440, Surfynol 465, and Surfynol 485 from Air Products and Chemicals Inc. and Surfynol E1004 from Nisshin Chemical Industry K.K.

The acetylene alcohol derivative is added in an amount of 0.01 to 2%, more preferably 0.02 to 1% by weight based on 100% by weight of the resist composition. Less than 0.01% by weight of the acetylene alcohol derivative would be ineffective for improving coating and shelf stability whereas more than 2% by weight would result in a resist composition with low resolution.

The present invention also provides a resist composition comprising

- (A) the above-defined organic solvent,
- (B) as a base resin, the silicone polymer of formula (1) in which some of the hydrogen atoms of the carboxyl groups or the carboxyl groups and the hydroxyl groups may be replaced by acid labile groups,
- (C) the above-defined photoacid generator, and
- (H) a crosslinkable compound by the action of acid.

Examples of the crosslinkable compound include epoxy compounds and urea compound as shown below.



The crosslinkable compound may preferably be blended in an amount of 5 to 95 parts by weight, more preferably 15 to 85 parts by weight, most preferably 20 to 75 parts

by weight per 100 parts by weight of the base resin. With less than 5 parts of the compound on this basis, crosslinking reaction would take place to an insufficient extent, tending to invite a lowering of film retentivity and allow winding and swelling of the pattern. More than 95 parts of the compound would leave more scum, adversely affecting development.

In the resist composition of the invention, a surface-active agent commonly used for facilitating coating may be blended as an optional component in addition to the aforementioned components. The amounts of such optional additives blended are conventional insofar as the objects of the invention are not impaired.

Nonionic surfactants are preferred. Examples of the surfactant include perfluoroalkylpolyoxyethylene ethanols, fluorinated alkyl esters, perfluoroalkylamine oxides, perfluoroalkyl EO addition products, and fluorinated organosiloxane compounds. Useful surfactants are commercially available under the trade name of Florade FC-430 and FC-431 from Sumitomo 3M K.K., Surflon S-141 and S-145 from Asahi Glass K.K., Unidine DS-401, DS-403 and DS-451 from Daikin Industry K.K., Megafac F-8151 from Dai-Nippon Ink & Chemicals K.K., and X-70-092 and X-70-093 from Shin-Etsu Chemical Co., Ltd. Preferred surfactants are Florade FC-430 from Sumitomo 3M K.K. and X-70-093 from Shin-Etsu Chemical Co., Ltd.

Any well-known lithography may be used to form a resist pattern from a resist composition of the invention. For example, the resist composition is applied to a substrate such as a silicon wafer so as to provide a film thickness of 0.5 to 2.0 μm by a technique such as spin coating, and prebaked on a hot plate at a temperature of 60 to 150°C for 1 to 10 minutes, preferably 80 to 120°C for 1 to 5 minutes. With a mask having a desired pattern placed above the resist film, the resist film is then exposed to actinic radiation having a wavelength of up to 300 nm such as deep-UV, excimer laser light, and X-ray or

electron beam in an exposure dose of about 1 to 200 mJ/cm², preferably about 10 to 100 mJ/cm². The film is further baked on a hot plate at 60 to 150°C for 1 to 5 minutes, preferably 80 to 120°C for 1 to 3 minutes (post-exposure baking = PEB). Thereafter the resist film is developed with a developer in the form of an aqueous base solution, for example, 0.1 to 5%, preferably 2 to 3% aqueous solution of tetramethylammonium hydroxide (TMAH) for 0.1 to 3 minutes, preferably 1/2 to 2 minutes by a conventional technique such as dipping, puddling or spraying. In this way, a desired positive resist pattern is formed on the substrate. The resist composition of the invention is best suited for fine patterning with actinic radiation, especially radiation having a wavelength of 254 to 193 nm such as deep-UV, excimer laser light, and X-ray and electron beam. Outside the upper and lower limits of the range, a failure to provide the desired pattern can occur.

The resist material of the invention is useful as a two-layer resist since it uses a silicone polymer as the base resin and is fully resistant to oxygen plasma etching.

More particularly, in a conventional way, a relatively thick organic polymer layer is formed on a substrate as a lower resist layer before a resist solution formulated according to the invention is spin coated thereon. The upper resist film of the invention is patterned as above. On subsequent etching, the lower resist layer is selectively etched away whereby the pattern of the upper resist layer is formed in the lower resist layer.

For the lower resist layer, a novolak resin based positive resist composition may be used. After it is coated onto a substrate, it is subject to hard baking at 200°C for one hour, thereby preventing intermixing with the silicone resist.

The resist composition comprising the silicone polymer as a base resin according to the invention is sensitive to actinic radiation, has superior sensitivity and resolution, and lends itself to fine processing technology using electron beam and deep-UV radiation. Because of very low absorption at the exposure wavelength of a ArF excimer laser or KrF excimer laser, the resist composition forms a fine pattern having a wall perpendicular to the substrate. Because the resist composition of the invention has high oxygen plasma etching resistance, a two-layer resist having a resist film of the invention coated on a lower resist layer can be finely patterned at a high aspect ratio.

EXAMPLE

Synthesis Examples and Examples are given below for illustrating the present invention although the invention is not limited thereto.

Synthesis Example 1: Synthesis of poly(3-carboxycyclohexylsilsesquioxane)

In 150 g of toluene was dissolved 150.0 g (0.544 mol) of methyl 3-trichlorosilyl-1-cyclohexylcarboxylate. With stirring, the solution was added dropwise to 300 g of water at room temperature. After the completion of dropwise addition, the acidic aqueous layer was separated from the reaction mixture. The organic layer was then washed with 1 liter of water. After the water layer became neutral, the organic layer was two more times washed with water. The solvent was distilled off from the organic layer by means of an evaporator. The concentrate was heated at 200°C for 2 hours for effecting polymerization. To the polymer was added 800 g of tetrahydrofuran. The resulting solution was added dropwise to 1,000 g of a 10% aqueous solution of sodium hydroxide, which was heated at 40°C for 3 hours for effecting hydrolysis of methyl ester groups. The reaction

solution was made acidic with hydrochloric acid whereupon the polymer precipitated. The polymer was collected by filtration and dried, obtaining poly(3-carboxycyclohexylsilsesquioxane) in a yield of 83.4 g. The polymer had a weight average molecular weight of 3,000.

Synthesis Example 2: Synthesis of poly[(3-carboxycyclohexylsilsesquioxane)-(cyclohexylsilsesquioxane)]

In 150 g of toluene were dissolved 75.0 g (0.272 mol) of methyl 3-trichlorosilyl-1-cyclohexylcarboxylate and 59.2 g (0.272 mol) of cyclohexyltrichlorosilane. With stirring, the solution was added dropwise to 300 g of water at room temperature. After the completion of dropwise addition, the acidic aqueous layer was separated from the reaction mixture. The organic layer was then washed with 1 liter of water. After the water layer became neutral, the organic layer was two more times washed with water. The solvent was distilled off from the organic layer by means of an evaporator. The concentrate was heated at 200°C for 2 hours for effecting polymerization. To the polymer was added 800 g of tetrahydrofuran. The resulting solution was added dropwise to 1,000 g of a 10% aqueous solution of sodium hydroxide, which was heated at 40°C for 3 hours for effecting hydrolysis of methyl ester groups. The reaction solution was made acidic with hydrochloric acid whereupon the polymer precipitated. The polymer was collected by filtration and dried, obtaining poly[(3-carboxycyclohexylsilsesquioxane)-(cyclohexylsilsesquioxane)] in a yield of 82.0 g. The polymer had a weight average molecular weight of 3,500. On ¹H-NMR analysis of the polymer, the compositional ratio of 3-carboxycyclohexylsilsesquioxane to cyclohexylsilsesquioxane was 50/50 (molar ratio).

Synthesis Examples 3-8

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In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 1. A catalytic amount of p-toluenesulfonic acid was added. With stirring at 20°C, 15.0 g of ethyl vinyl ether was added. After one hour of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained, 60 g, was dissolved in 560 ml of tetrahydrofuran, to which 34.0 g of 1-hydrobenzotriazole and 31.6 g of diisopropylcarbodiimide were added and thereafter, 7.7 g of ethanol amine was added. After reaction at 30°C for 5 hours, the reaction solution was concentrated and added dropwise to 3 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 50 ml of acetone, which was added dropwise to 3 liters of water. After filtration, the

polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.1) shown below. It was ascertained from $^1\text{H-NMR}$ analysis that 50% of the hydrogen atoms of carboxyl groups in the polymer were ethoxyethylated and 50% replaced by $-\text{NHCH}_2\text{CH}_2\text{OH}$.

Synthesis Example 10

In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 1. A catalytic amount of p-toluenesulfonic acid was added. With stirring at 20°C , 12.0 g of ethylene 1-propenyl ether was added dropwise. After 2 hours, 8.7 g of 1,4-butanediol divinyl ether was added dropwise. After 30 minutes of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained, 60 g, was dissolved in 560 ml of tetrahydrofuran, to which 34.0 g of 1-hydrobenzotriazole and 31.6 g of diisopropylcarbodiimide were added and thereafter, 26.3 g of 2-amino-2-methyl-1,3-propanediol was added. After reaction at 30°C for 5 hours, the reaction solution was concentrated and added dropwise to 3 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 50 ml of acetone, which was added dropwise to 3 liters of water. After filtration, the polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.2) shown below. It was ascertained from $^1\text{H-NMR}$ analysis that 40% of the hydrogen atoms of carboxyl groups in the polymer were ethoxypropylated, 20% crosslinked and 40% replaced by $-\text{NHC}(\text{CH}_3)(\text{CH}_2\text{OH})_2$.

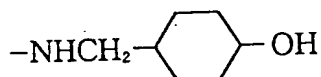
Synthesis Examples 11-18

Silicone polymers represented by the following rational formulae (Polym.3 to 10) were obtained by

following the procedures of Synthesis Examples 9 and 10 except for the following changes. Each of the polymers of Synthesis Examples 1 to 8 was used. Compounds capable of introducing an acid labile group as shown in Polym. 3 to 10 and a group of the general formula (2b) were used instead of the ethyl vinyl ether and ethanol amine. 1,4-bis[(vinylloxy)methyl]cyclohexane was used instead of the 1,4-butanediol divinyl ether.

10 Synthesis Example 19

In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 1. To the solution, 69.7 g of trifluoroacetic anhydride was added, and with stirring at 20°C, 17.2 g of t-butyl alcohol was added. After 5 hours of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained, 60 g, was dissolved in 560 ml of tetrahydrofuran, to which 34.0 g of 1-hydrobenzotriazole and 31.6 g of diisopropylcarbodiimide were added and thereafter, 19.5 g of 4-aminomethyl-1-cyclohexanol was added. After reaction at 30°C for 5 hours, the reaction solution was concentrated and added dropwise to 3 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 50 ml of acetone, which was added dropwise to 3 liters of water. After filtration, the polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.11) shown below. It was ascertained from ¹H-NMR analysis that 40% of the hydrogen atoms of carboxyl groups in the polymer were tert-butylated and 60% replaced by groups of the following formula.



Synthesis Example 20

By following the procedure of Synthesis Example 19 except that the polymer of Synthesis Example 2 was used and 3-amino-1,2-propanediol was used instead of the 4-aminomethyl-1-cyclohexanol, a silicone polymer represented by the following rational formula (Polym.12) was obtained.

10 Synthesis Example 21

By following the procedure of Synthesis Example 19 except that the polymer of Synthesis Example 6 was used and 2-(2-aminoethoxy)ethanol was used instead of the 1-aminomethyl-1-cyclohexanol, a silicone polymer represented by the following rational formula (Polym.13) was obtained.

Synthesis Example 22

In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 1. A catalytic amount of p-toluenesulfonic acid was added. With stirring at 20°C, 21.5 g of ethyl 1-propenyl ether was added dropwise. After 2 hours of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained, 60 g, was dissolved in tetrahydrofuran, to which potassium carbonate was added in solid form. With stirring, 27.8 g of bromoethanol was added. After reaction at 60°C for 6 hours, the solid potassium carbonate was removed from the reaction solution by filtration. From the filtrate, the solvent and unreacted bromoethanol were distilled off in vacuum. The residue was dissolved in acetone and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 200 ml of acetone,

which was added dropwise to 3 liters of water. After filtration, the polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.14) shown below. It was ascertained from $^1\text{H-NMR}$ analysis that 60% of the hydrogen atoms of carboxyl groups in the polymer were ethoxypropylated and 40% replaced by $-\text{OCH}_2\text{CH}_2\text{OH}$.

Synthesis Example 23

By following the procedure of Synthesis Example 20 except that the polymer of Synthesis Example 6 was used, a silicone polymer represented by the following rational formula (Polym.15) was obtained.

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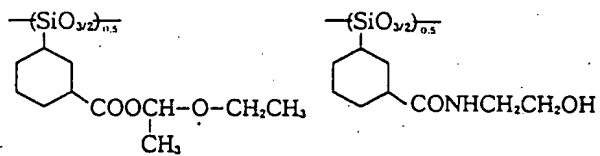
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Polym.1

Mw = 4,000

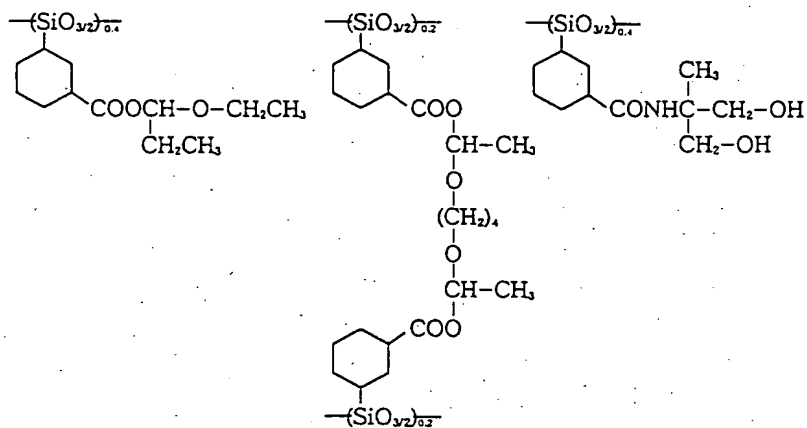
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Polym.2

Mw = 12,000

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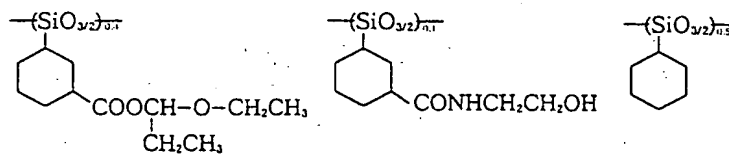
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Polym.3

Mw = 4,300

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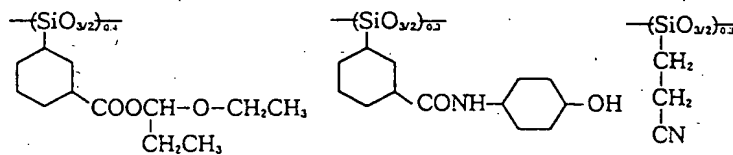


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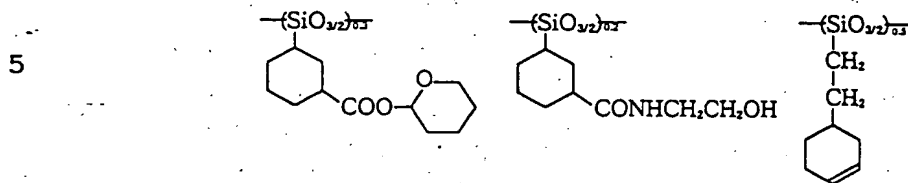
Polym.4

Mw = 4,600

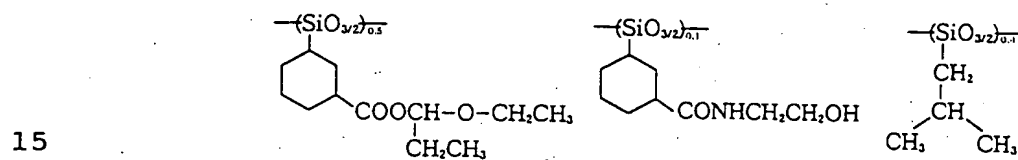
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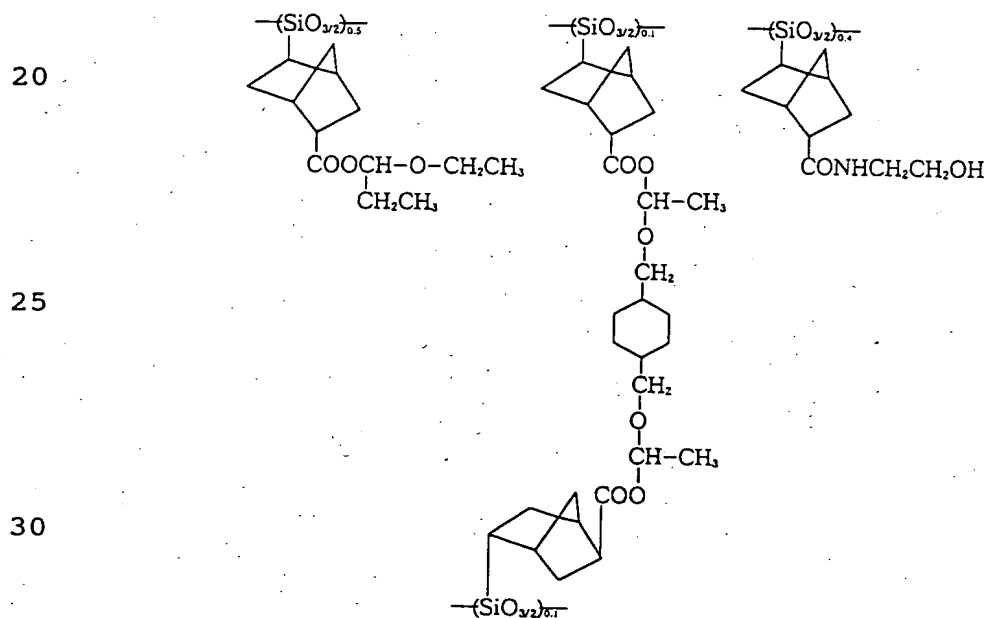
Polym.5 Mw = 14,300



Polym.6 Mw = 4,200

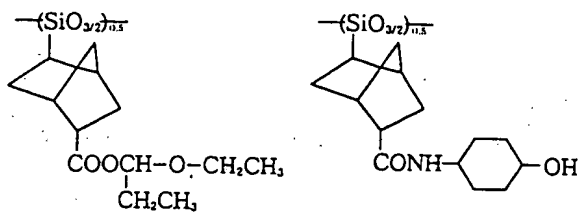


Polym.7 Mw = 15,000



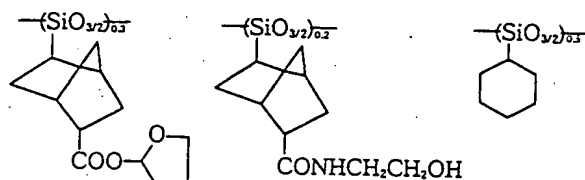
Polym.8

Mw = 5,000



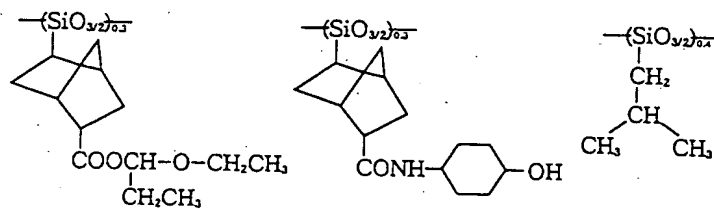
Polym.9

Mw = 5,400



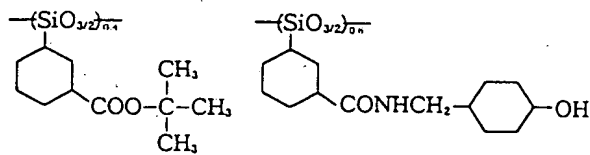
Polym.10

Mw = 4,520



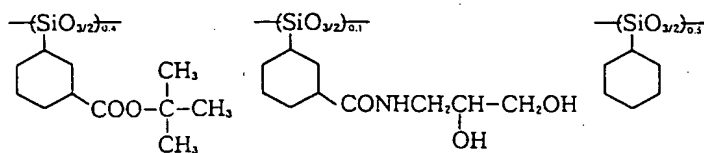
Polym.11

Mw = 4,300

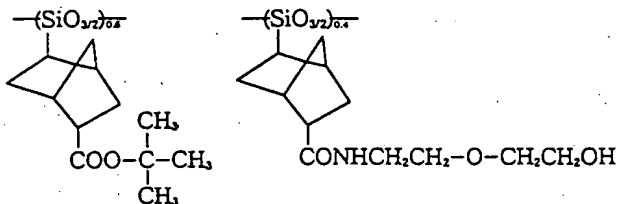


Polym.12

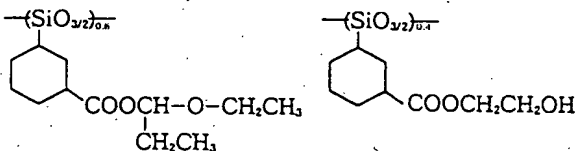
Mw = 4,100



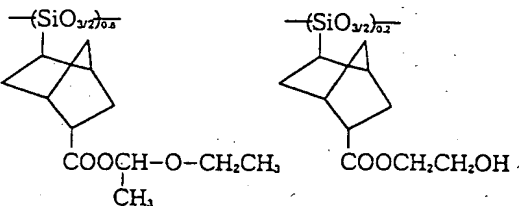
Polym.13 Mw = 4,660



Polym.14 Mw = 4,200



Polym.15 Mw = 4,650



Synthesis Example 24: Synthesis of poly[(3-carboxycyclohexylsilsesquioxane)-(8-hydroxy-4-tricyclo[5.2.1.0^{2.6}]-decanylsilsesquioxane)]

In 150 g of toluene were dissolved 75.0 g (0.272 mol) of methyl 3-trichlorosilyl-1-cyclohexylcarboxylate and 89.1 g (0.272 mol) of 8-acetoxy-4-trichlorosilyltricyclo[5.2.1.0^{2.6}]decane. With stirring, the solution was added dropwise to 300 g of water at room temperature. After the completion of dropwise addition, the acidic aqueous layer was separated from the reaction mixture. The organic

layer was then washed with 1 liter of water. After the water layer became neutral, the organic layer was two more times washed with water. The solvent was distilled off from the organic layer by means of an evaporator. The concentrate was heated at 200°C for 2 hours for effecting polymerization. To the polymer was added 800 g of tetrahydrofuran. The resulting solution was added dropwise to 1,000 g of a 10% aqueous solution of sodium hydroxide, which was heated at 40°C for 3 hours for effecting hydrolysis of methyl ester and acetoxy groups. The reaction solution was made acidic with hydrochloric acid whereupon the polymer precipitated. The polymer was collected by filtration and dried, obtaining poly[(3-carboxycyclohexylsilsesquioxane)-(8-hydroxy-4-tricyclo[5,2,1,0^{2,6}]decanylsilsesquioxane)] in a yield of 98.6 g. The polymer had a weight average molecular weight of 4,000. On ¹H-NMR analysis of the polymer, the compositional ratio of 3-carboxycyclohexylsilsesquioxane to 8-hydroxy-4-tricyclo[5,2,1,0^{2,6}]decanylsilsesquioxane was 50/50 (molar ratio).

Synthesis Example 25: Synthesis of poly[(3-carboxycyclohexylsilsesquioxane)-(8-hydroxy-4-tricyclo[5,2,1,0^{2,6}]decanylsilsesquioxane)-(cyclohexylsilsesquioxane)]

In 150 g of toluene were dissolved 60.1 g (0.218 mol) of methyl 3-trichlorosilyl-1-cyclohexylcarboxylate, 71.4 g (0.218 mol) of 8-acetoxy-4-trichlorosilyltricyclo[5,2,1,0^{2,6}]decane and 23.7 g (0.109 mol) of cyclohexyltrichlorosilane. With stirring, the solution was added dropwise to 300 g of water at room temperature. After the completion of dropwise addition, the acidic aqueous layer was separated from the reaction mixture. The organic layer was then washed with 1 liter of water. After the water layer became neutral, the organic layer was two more times washed with water. The solvent was distilled off from the organic layer by means of an evaporator. The concentrate was heated at 200°C for 2 hours for effecting

polymerization. To the polymer was added 800 g of tetrahydrofuran. The resulting solution was added dropwise to 1,000 g of a 10% aqueous solution of sodium hydroxide, which was heated at 40°C for 3 hours for effecting hydrolysis of methyl ester and acetoxy groups. The reaction solution was made acidic with hydrochloric acid whereupon the polymer precipitated. The polymer was collected by filtration and dried, obtaining poly[(3-carboxycyclohexylsilsesquioxane)-(8-hydroxy-4-tricyclo[5,2,1,0^{2,6}]decanyl-silsesquioxane)-(cyclohexyl-silsesquioxane)] in a yield of 83.4 g. The polymer had a weight average molecular weight of 5,000. On ¹H-NMR analysis of the polymer, the compositional ratio of 3-carboxycyclohexylsilsesquioxane/8-hydroxy-4-tricyclo[5,2,1,0^{2,6}]decanyl-silsesquioxane/cyclohexylsilsesquioxane was 40/40/20 (molar ratio).

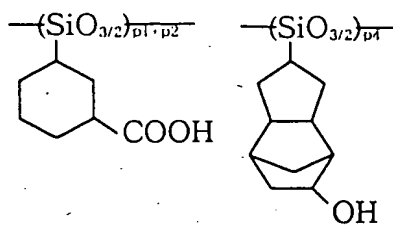
Synthesis Examples 26-31

Silicone polymers as shown in Table 2 were obtained by the same procedure as in Synthesis Examples 24 and 25. The thus obtained polymers had the weight average molecular weight and compositional ratio shown in Table 2.

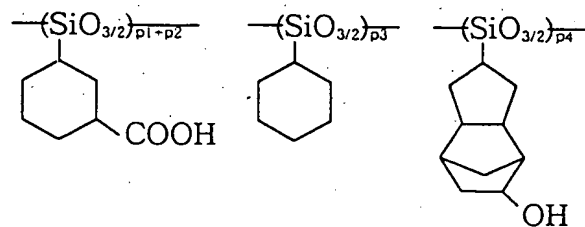
Table 2

Synthesis Example	Polymer prior to introduction of acid labile group		
	Polymer	(p1+p2)/p3/p4 (molar ratio)	Mw
24	(I)	50/0/50	4,000
25	(J)	40/20/40	5,000
26	(K)	30/30/40	2,600
27	(L)	70/0/30	3,500
28	(M)	40/0/60	3,000
29	(N)	50/20/30	5,400
30	(O)	40/40/20	3,200
31	(I)	60/0/40	3,700

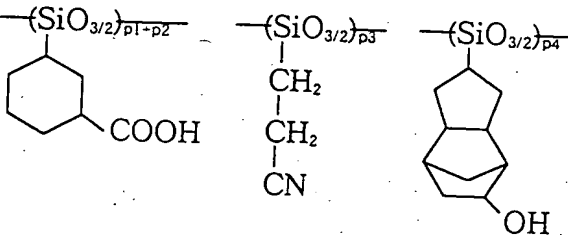
(I)



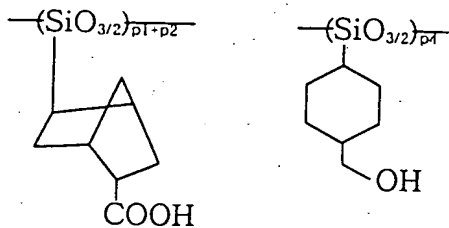
(J)



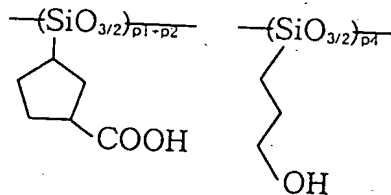
(K)



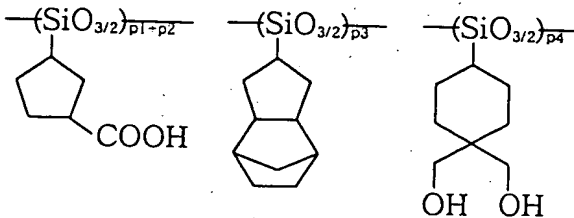
(L)

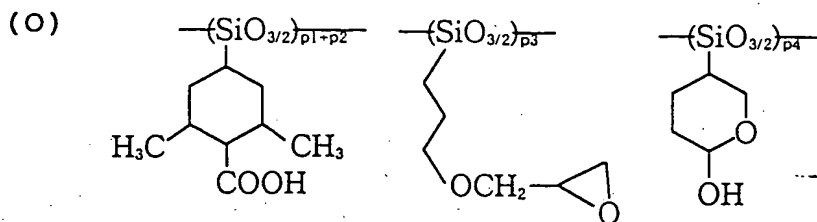


(M)



(N)





Synthesis Example 32

In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 24. A catalytic amount of p-toluenesulfonic acid was added. With stirring at 20°C, 10.8 g of ethyl vinyl ether was added. After one hour of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained had the structure of the rational formula (Polym.16) shown below. It was ascertained from ¹H-NMR analysis that 90% of the hydrogen atoms of carboxyl groups in the polymer were ethoxyethylated.

Synthesis Example 33

In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 31. A catalytic amount of p-toluenesulfonic acid was added. With stirring at 20°C, 8.7 g of ethyl vinyl ether was added dropwise. After 1 hour of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained, 60 g, was dissolved in 540 ml of tetrahydrofuran, to which 27.0 g of 1-hydroxybenzotriazole and 12.6 g of N,N'-diisopropylcarbodiimide were added and

thereafter, 6.1 g of ethanol amine was added. After reaction at 30°C for 5 hours, the reaction solution was concentrated and added dropwise to 3 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 50 ml of acetone, which was added dropwise to 3 liters of water. After filtration, the polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.17) shown below. It was ascertained from ¹H-NMR analysis that 60% of the hydrogen atoms of carboxyl groups in the polymer were ethoxyethylated and 30% replaced by -NHCH₂CH₂OH.

Synthesis Example 34

In 450 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 31. A catalytic amount of p-toluenesulfonic acid was added. With stirring at 20°C, 6.9 g of ethylene 1-propenyl ether was added dropwise. After 2 hours, 5.7 g of 1,4-butanediol divinyl ether was added dropwise. After 30 minutes of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer thus obtained, 60 g, was dissolved in 540 ml of tetrahydrofuran, to which 27.0 g of 1-hydroxybenzotriazole and 12.6 g of N,N'-diisopropylcarbodiimide were added and thereafter, 10.5 g of 2-amino-2-methyl-1,3-propanediol was added. After reaction at 30°C for 5 hours, the reaction solution was concentrated and added dropwise to 3 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 50 ml of acetone, which was added dropwise to 3 liters of water. After filtration, the polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.18) shown below. It was ascertained from ¹H-NMR analysis that 40% of the

hydrogen atoms of carboxyl groups in the polymer were ethoxypropylated, 20% crosslinked and 30% replaced by $\text{-NHC(CH}_3\text{)(CH}_2\text{OH)}_2$.

5 Synthesis Examples 35-41

Silicone polymers represented by the following rational formulae (Polym.19 to 25) were obtained by following the procedures of Synthesis Examples 32,33 and 34 except for the following changes. Each of the polymers of Synthesis Examples 26 to 33 was used. Compounds capable of introducing an acid labile group as shown in Polym.19 to 25 and a group of the general formula (2a) or (2b) were used instead of the ethyl vinyl ether and ethanol amine. 1,4-bis[(vinylloxy)methyl]cyclohexane was used instead of the 1,4-butanediol divinyl ether.

Synthesis Example 42

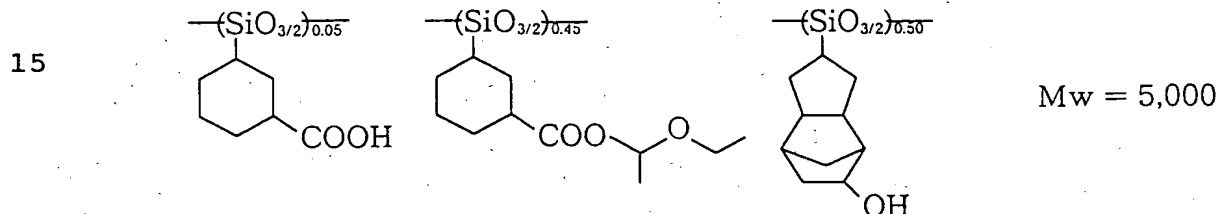
In 200 ml of dimethylformamide was dissolved 20 g of the polymer obtained in Synthesis Example 24. Potassium carbonate was added thereto in solid form. With stirring, 15.1 g of tert-butyl chloroacetate was added. Reaction was conducted at 60°C for 6 hours. The solid potassium carbonate was filtered off from the reaction solution, to which 10 liters of water was added dropwise, yielding a white solid. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. Filtration and vacuum drying yielded a polymer. The polymer had the structure of the rational formula (Polym.26) shown below. It was ascertained from $^1\text{H-NMR}$ analysis that 60% of the hydrogen atoms of carboxyl groups in the polymer were tert-butoxycarbonylmethylated.

Synthesis Example 43

In 180 ml of tetrahydrofuran was dissolved 50 g of the polymer obtained in Synthesis Example 24. To the solution, 52.5 g of trifluoroacetic anhydride was added, and with stirring below 5°C, 18.5 g of t-butyl alcohol was

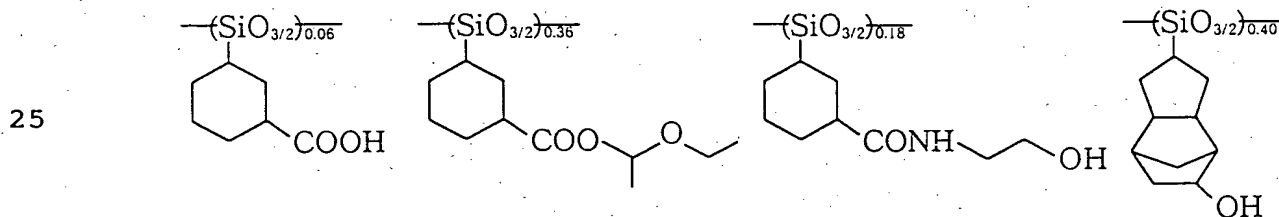
added. After 2 hours of reaction, the reaction solution was neutralized with conc. aqueous ammonia and added dropwise to 5 liters of water whereupon a white solid formed. After filtration, the solid was dissolved in 100 ml of acetone, which was added dropwise to 5 liters of water. After filtration, the polymer was dried in vacuum. The polymer had the structure of the rational formula (Polym.27) shown below. It was ascertained from ¹H-NMR analysis that 80% of the hydrogen atoms of carboxyl groups in the polymer were tert-butylated.

Polym. 16



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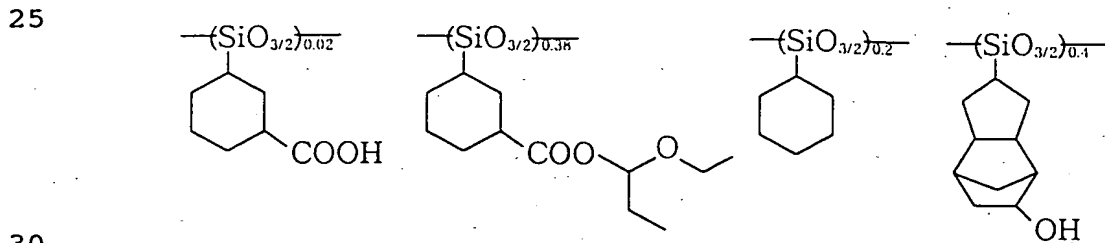
Polym. 17



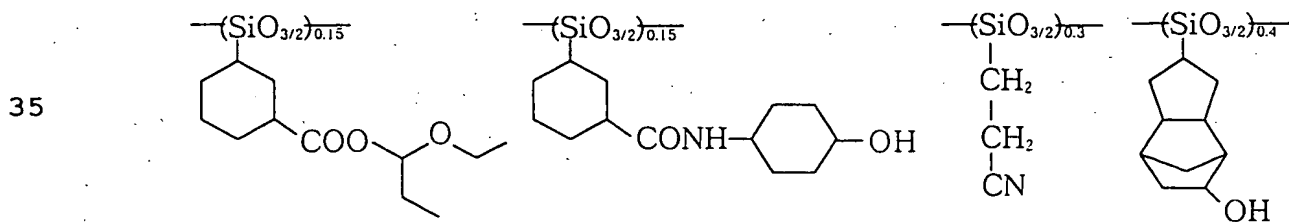
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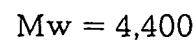
Polym. 19



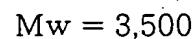
Polym. 20


$$M_w = 3,400$$

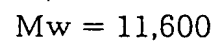
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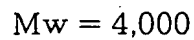


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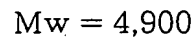


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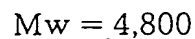
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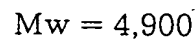
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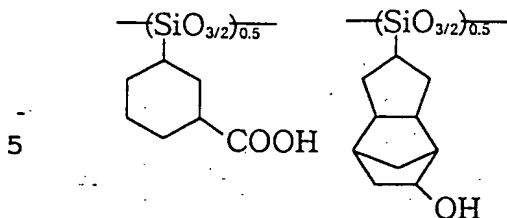


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Polym. 28



Mw = 4,000

10 Examples 1-28

Liquid resist compositions were prepared by using polymers (Polym.1 to Polym.15) obtained in the foregoing Synthesis Examples as a base resin, and dissolving a photoacid generator designated PAG.1 to PAG.5, a dissolution inhibitor designated DRR.1 and DRR.2, a basic compound, and an aromatic compound having a group $\equiv\text{C-COOH}$ in a molecule designated ACC.1 in propylene glycol monoethyl acetate (PGMEA), ethyl lactate (EL) or diethylene glycol monomethyl ether (DGLYME) in accordance with the formulation shown in Table 3. Each of the compositions was passed through a 0.2- μm Teflon filter.

The thus obtained liquid resist composition was spin coated onto a silicon wafer to a thickness of 0.3 μm . With the silicon wafer rested on a hot plate, the coating was pre-baked at 100°C for 90 seconds. The film was exposed to light by means of an ArF excimer laser stepper (manufactured by Nikon K.K., NA = 0.55), baked at 110°C for 90 seconds, and developed with an aqueous solution of 2.38% tetramethylammonium hydroxide, obtaining a pattern. The resulting resist pattern was evaluated as follows. The results are shown in Tables 3 and 4.

Test methods

First, a sensitivity was determined. Provided that the exposure dose with which a 0.20- μm line-and-space pattern was resolved at 1:1 was the optimum exposure dose (Eop), the minimum line width of a line-and-space pattern which was recognized separate at this exposure dose was

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(PAG.5)



Table 3

No.	Resist composition (compositional ratio in parentheses, unit: pbw)					Sensitivity: Eop (mJ/cm ²)	Resolution (μ m)	Profile	Edge roughness (nm)
	Base resin	Photoacid generator	Dissolution inhibitor	Basic compound	Solvent				
1	Polym.1 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.1	0.16	rectangular	5
2	Polym.2 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.2	0.16	rectangular	5
3	Polym.3 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.1	0.18	rectangular	7
4	Polym.4 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	6.0	0.18	rectangular	7
5	Polym.5 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.2	0.16	rectangular	5
6	Polym.6 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.2	0.16	rectangular	5
7	Polym.7 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	6.7	0.16	rectangular	4
8	Polym.8 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.8	0.15	rectangular	3
9	Polym.9 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	7.2	0.16	rectangular	5
10	Polym.10 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	6.2	0.16	rectangular	5
11	Polym.11 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.1	0.16	rectangular	6
12	Polym.12 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	6.1	0.18	rectangular	8
13	Polym.13 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	6.3	0.18	rectangular	10
14	Polym.14 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	7.9	0.18	rectangular	8
15	Polym.15 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	8.1	0.18	rectangular	9

Table 4

No.	Resist composition (compositional ratio in parentheses, unit: pbw)					Sensitivity: Eop (mJ/cm ²)	Resolution (μ m)	Profile	Edge roughness (nm)
	Base resin	Photoacid generator	Dissolution inhibitor	Basic compound	Other additives				
16	Polym.1 (98)	PAG.2 (2)	-	-	-	4.5	0.17	rectangular	5
17	Polym.1 (98)	PAG.3 (2)	-	-	-	15	0.17	rectangular	7
18	Polym.1 (98)	PAG.4 (2)	-	-	-	9.5	0.17	rectangular	7
19	Polym.1 (98)	PAG.5 (2)	-	-	-	4.5	0.17	rectangular	5
20	Polym.1 (98)	PAG.1 (2)	DRI.1 (16)	-	-	5.5	0.17	rectangular	7
21	Polym.1 (82)	PAG.5 (2)	DRI.2 (16)	-	-	5.5	0.17	rectangular	7
22	Polym.1 (98)	PAG.1 (2)	-	triethanolamine (0.1)	-	6.2	0.16	rectangular	4
23	Polym.1 (98)	PAG.1 (2)	-	N- methylpyrrolidone (0.05)	-	1	0.20	rectangular	10
24	Polym.1 (82)	PAG.1 (2)	DRI.1 (16)	quinoline (0.05)	-	1.8	0.20	rectangular	9
25	Polym.1 (98)	PAG.1 (2)	-	tributylamine (0.1) piperidine ethanol (0.05)	-	7.2	0.16	rectangular	6
26	Polym.1 (98)	PAG.1 (2)	DRI.1 (16)	quinoline (0.05)	ACC.1 (0.05)	2.0	0.18	rectangular	7
27	Polym.1 (98)	PAG.2 (2)	-	-	-	4.5	0.17	rectangular	5
28	Polym.1 (98)	PAG.2 (2)	-	-	-	4.5	0.17	rectangular	5

It is evident from Tables 3 and 4 that resist compositions of the invention form resist patterns having a high resolution and free of asperities (having a minimized edge roughness).

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Example 29

A silicon wafer was coated with a lower resist film of 2.0 μm thick using OFPR 800 (Tokyo Oka K.K.), and the film was cured by heating at 200°C for 5 minutes. The resist composition used in Example 1 was similarly coated onto the lower resist film to a thickness of about 0.35 μm and pre-baked. The resist film was then exposed to a KrF excimer laser beam and developed, forming a pattern on the lower resist film. The resist composition could form a pattern having perpendicular side walls on the lower resist film without footing.

Using a parallel plate type sputter etching apparatus, the resist was etched with oxygen gas as an etchant gas. The lower resist film was etched at a rate of 150 nm/min. while the inventive resist film was etched at a rate of less than 15 nm/min. After 15 minutes of etching, those portions of the lower resist film which were not covered with the inventive resist film were completely eliminated, leaving a two-layer resist pattern having a thickness of more than 1 μm . The etching conditions are shown below.

Gas flow rate: 50 SCCM
Gas pressure: 1.3 Pa
RF power: 50 W
DC bias: 450 V

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Examples 36-64

Liquid resist compositions were prepared by using polymers (Polym.16 to Polym.28) obtained in the foregoing Synthesis Examples as a base resin, and dissolving a photoacid generator designated PAG.1 to PAG.8, a dissolution inhibitor designated DRR.1 to DRR.4, a basic

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compound, a compound having a group =C-COOH in a molecule designated ACC.1 and a compound crosslinkable by the action of acid designated Crosslinker 1 and Crosslinker 2 in a solvent containing 0.05% by weight of FC-430 (Sumitomo 3M K.K.) in accordance with the formulation shown in Tables 5-7. Each of the compositions was passed through a 0.2- μm Teflon filter.

The thus obtained liquid resist composition was spin coated onto a silicon wafer to a thickness of 0.3 μm .

With the silicon wafer rested on a hot plate, the coating was pre-baked at 100°C for 90 seconds. The film was exposed to light by means of an ArF excimer laser stepper (manufactured by Nikon K.K., NA = 0.55), baked at 110°C for 90 seconds (PEB), and developed with an aqueous solution of 2.38% tetramethylammonium hydroxide, obtaining a pattern. The resulting resist pattern was evaluated as follows. The results are shown in Tables 5-7.

Test methods

First, a sensitivity was determined. Provided that the exposure dose with which a 0.20- μm line-and-space pattern was resolved at 1:1 was the optimum exposure dose (Eop), the minimum line width of a line-and-space pattern which was recognized separate at this exposure dose was the resolution of a test resist. The profile of the resist pattern resolved was observed under a scanning electron microscope. The edge roughness of a 0.20- μm line-and-space pattern was also observed under a micrometer-built-in scanning electron microscope S7280 (Hitachi K.K.).





Weight average molecular
weight: 3,000

CC(Cc1ccc(O)cc1)c2ccc(O)cc2CC(=O)OCOCN1C(=O)N(COC)C(=O)N1COCCOCN1C(=O)N(COC)C(OC)C1OC

(Crosslinker 2)

Table 5

No.	Resist composition (compositional ratio in parentheses, unit: pbw)					Sensitivity: Eop (mJ/cm ²)	Resolution (μ m)	Profile	Edge roughness (nm)
	Base resin	Photoacid generator	Dissolution inhibitor	Basic compound	Solvent				
30	Polym.16 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	4.8	0.16	rectangular	5
31	Polym.17 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.5	0.17	rectangular	5
32	Polym.18 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.2	0.15	rectangular	4
33	Polym.19 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.0	0.16	rectangular	5
34	Polym.20 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	4.5	0.16	rectangular	5
35	Polym.21 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	6.0	0.16	rectangular	5
36	Polym.22 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	4.5	0.18	rectangular	7
37	Polym.23 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.2	0.16	rectangular	5
38	Polym.24 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	5.0	0.18	rectangular	7
39	Polym.25 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	4.5	0.16	rectangular	5
40	Polym.26 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	7.2	0.17	rectangular	5
41	Polym.27 (98)	PAG.1 (2)	-	tributylamine (0.1)	PGMEA (600)	7.5	0.17	rectangular	5

Table 6

No.	Resist composition (compositional ratio in parentheses, unit: pbw)					Sensitivity: Eop (mJ/cm ²)	Resolution (μm)	Profile	Edge roughness (nm)
	Base resin	Photoacid generator	Dissolution inhibitor	Basic compound	Solvent				
42	Polym.16 (98)	PAG.1 (2)	-	triethanolamine (0.1)	PGMEA (600)	5.0	0.16	rectangular	5
43	Polym.16 (98)	PAG.1 (2)	-	N-methylpyrrolidone (0.05)	PGMEA (600)	2.3	0.18	rectangular	9
44	Polym.16 (98)	PAG.1 (2)	-	quinoline (0.05)	PGMEA (600)	1.8	0.18	rectangular	9
45	Polym.16 (98)	PAG.1 (2)	-	tributylamine (0.1) piperidine ethanol (0.05)	PGMEA (600)	7.2	0.16	rectangular	7
46	Polym.16 (98)	PAG.1 (2)	-	trisethoxymethoxy- ethylamine (0.15)	PGMEA (600)	5.2	0.15	rectangular	4
47	Polym.16 (98)	PAG.1 (2)	-	trisethoxyethoxy- methoxyethylamine (0.2)	PGMEA (600)	6.0	0.15	rectangular	4
48	Polym.16 (98)	PAG.1 (2)	DRR.1 (5)	tributylamine (0.1)	PGMEA (600)	4.0	0.16	rectangular	7
49	Polym.16 (98)	PAG.1 (2)	DRR.2 (5)	tributylamine (0.1)	PGMEA (600)	4.0	0.16	rectangular	7
50	Polym.16 (98)	PAG.1 (2)	DRR.3 (5)	tributylamine (0.1)	PGMEA (600)	8.0	0.18	rectangular	8
51	Polym.16 (98)	PAG.1 (2)	DRR.4 (5)	tributylamine (0.1)	PGMEA (600)	8.0	0.18	rectangular	8
52	Polym.16 (98)	PAG.2 (2)	-	tributylamine (0.1)	PGMEA (600)	3.0	0.18	rectangular	7
53	Polym.16 (98)	PAG.3 (2)	-	tributylamine (0.1)	PGMEA (600)	8.0	0.17	rectangular	8

Table 7

No.	Resist composition (compositional ratio in parentheses, unit: pbw)					Sensitivity: Eop (mJ/cm ²)	Resolution (μ m)	Profile	Edge roughness (nm)
	Base resin	Photoacid generator	Dissolution inhibitor	Basic compound	Solvent				
54	Polym.16 (98)	PAG.4 (2)	-	tributylamine (0.1)	PGMEA (600)	7.5	0.16	rectangular	6
55	Polym.16 (98)	PAG.5 (2)	-	tributylamine (0.1)	PGMEA (600)	8.5	0.17	rectangular	8
56	Polym.16 (98)	PAG.6 (2)	-	tributylamine (0.1)	PGMEA (600)	8.5	0.17	rectangular	8
57	Polym.16 (98)	PAG.7 (2)	-	tributylamine (0.1)	PGMEA (600)	2.3	0.18	rectangular	8
58	Polym.16 (98)	PAG.8 (2)	-	tributylamine (0.1)	PGMEA (600)	3.0	0.18	rectangular	7
59	Polym.16 (98)	PAG.1 (2)	ACC.1 (1)	tributylamine (0.1)	PGMEA (600)	4.0	0.16	rectangular	6
60	Polym.16 (98)	PAG.1 (2)	-	tributylamine (0.1)	EL (600)	4.2	0.16	rectangular	5
61	Polym.16 (98)	PAG.1 (2)	-	tributylamine (0.1)	EIPA (600)	4.8	0.16	rectangular	5
62	Polym.28 (98)	PAG.1 (2)	Crosslinker1	-	PGMEA (600)	8	0.18	rectangular	12
63	Polym.28 (98)	PAG.1 (2)	Crosslinker1	tributylamine (0.1)	PGMEA (600)	20	0.18	rectangular	10
64	Polym.28 (98)	PAG.1 (2)	Crosslinker2	tributylamine (0.1)	PGMEA (600)	20	0.18	rectangular	10

PGMEA: propylene glycol methyl ether acetate

EL: ethyl lactate

EIPA: 1-ethoxy-2-propanol

It is evident from Tables 5-7 that resist compositions of the invention form resist patterns having a high resolution and free of asperities (having a minimized edge roughness).

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Example 65

A silicon wafer was coated with a lower resist film of 1.0 μm thick using OFPR 800 (Tokyo Oka K.K.), and the film was cured by heating at 300°C for 5 minutes. The resist composition used in Example 30 was similarly coated onto the lower resist film to a thickness of about 0.3 μm and pre-baked. The resist film was then exposed to a KrF excimer laser beam and developed, forming a pattern on the lower resist film. The resist composition could form a pattern having perpendicular side walls on the lower resist film without footing.

Using a parallel plate type sputter etching apparatus, the resist was etched with oxygen gas as an etchant gas. The lower resist film was etched at a rate of 150 nm/min. while the inventive resist film was etched at a rate of less than 15 nm/min. After 15 minutes of etching, those portions of the lower resist film which were not covered with the inventive resist film were completely eliminated, leaving a two-layer resist pattern having a thickness of more than 1 μm . The etching conditions are shown below.

Gas flow rate: 50 SCCM
Gas pressure: 1.3 Pa
RF power: 50 W
DC bias: 450 V

Japanese Patent Application Nos. 224389/1997 and 052760/1998 are incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the

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appended claims, the invention may be practiced otherwise than as specifically described.

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